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Environmental Fates and Impacts of Major Forest Use Pesticides

TRW Environmental Engineering Div.
Redondo Beach, CA

Prepared for

Environmental Protection Agency
Washington, DC

Dec 81

U.S. Department of Commerce
National Technical Information Service
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ENVIRONMENTAL FATES AND IMPACTS OF MAJOR FOREST USE PESTICIDES

by:
Masood Ghassemi (Program Manager and Technical Director)
and
Linda Fargo, Page Painter, Pam Painter, Sandra Quinlivan, Robert Scofield and Anne Takata

December 1981

TRW *ENVIRONMENTAL DIVISION*
REDONDO BEACH, CA 90278

EPA Contract No. 68-02-3174
Work Assignment Nos. 13, 14 and 62

EPA Project Officer: Michael Dellarco

Prepared for:
U.S. Environmental Protection Agency
Office of Pesticides and Toxic Substances
Washington, D.C. 20460

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In January 1980, the Special Pesticide Review Division of the U.S. Environmental Protection Agency's Office of Pesticides and Toxic Substances initiated the 'Forest Use Chemicals Project', the objective of which was to develop guidance for the timber production industry and the public on the comparative risks and benefits associated with various chemical and non-chemical approaches to pest control in timber management. The report includes information on biodegradation and persistence of various pesticides in plant, air, soil and water environments, and on their potential hazard to non-target plants and organisms. The environmental fate and impact data presented in this document, in combination with estimates of potential for human exposure (e.g., due to drift from aerial applications) and animal/human toxicity data, provide the data base for assessing potential risks associated with the use of a specific pesticide.

KEYWORDS: *Pesticides, *Environmental impacts, *Forestry.

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PREFACE AND ACKNOWLEDGEMENTS

This compendium of environmental fate and impact profiles for major forestry pesticides is one output of the Forest Use Chemicals Project, a multi-contractor/grantee study sponsored by the Office of Pesticides and Toxic Substances (OPTS) of the U.S. Environmental Protection Agency and aimed at developing guidance for the timber production industry and public on comparative risks and benefits of various chemical and non-chemical approaches to pest management. Those on the TRW project staff wish to express their gratitude to the EPA Project Officer, Mr. Michael Dellarco, for his advice and guidance during the course of the program. Special thanks are also due to a number of EPA technical and management staff, specially to Mrs. Jan Auerbach, Chief of the Regulatory Support Branch, Special Pesticide Review Division of OPTS, who reviewed program progress and provided constructive suggestions and guidance.

Much of the data used in developing the pesticide profiles were supplied by individuals/companies engaged in pesticide characterization and related field studies. The project is deeply indebted to these supporting individuals/organizations, particularly to those listed in Table 2, and to the technical experts and pesticide registrants listed in Table 3, who reviewed and commented on the draft profiles.

At TRW, the Program Manager and Technical Director for the effort was Dr. Masood Ghassemi. The development of the data base for this compendium involved review and technical evaluation of a voluminous amount of data by individuals from several different technical disciplines; Mr. Irving Zuckerman, the General Manager of TRW Environmental Division, was most instrumental in assuring timely availability of appropriate technical talents to the program. Special thanks are also due to Mrs. Monique Tholke for typing the compendium and for her invaluable secretarial support to the project.

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1.0 BACKGROUND, OBJECTIVES AND SCOPE

In January 1980, the Special Pesticide Review Division of the U.S. Environmental Protection Agency's Office of Pesticides and Toxic Substances initiated the "Forest Use Chemicals Project", the objective of which was to develop guidance for the timber production industry and the public on the comparative risks and benefits associated with various chemical and non-chemical approaches to pest control in timber management. A key impetus for the project was the ban imposed on the forestry uses of herbicide 2,4,5-T, thereby precipitating considerable interest in examining chemical and non-chemical alternatives to the use of 2,4,5-T.

Since the fate in the environment and the potential impacts on non-target plants and animals are important considerations in assessing the relative safety and environmental suitability of pesticides, in developing the data base for risk analysis in the Forest Use Chemicals Project, a considerable effort was devoted to the compilation and review of the available data on environmental fate and impact of some eighteen pesticides addressed in the study. The collected data and the results are presented in this compendium which is also intended as an "information transfer" document, thereby making available to the practicing foresters, state and local regulatory agencies, and the public interested in the safe use of pesticides, the most up-to-date information on biodegradation and persistence of various pesticides in plant, air, soil and water environments, and on their potential hazard to non-target plants and organisms. The document also draws attention to major gaps and conflicts in the existing data so that appropriate testing and field studies can be designed to generate the additional data. The environmental fate and impact data presented in this document, in combination with estimates of potential for human exposure (e.g., due to drift from aerial applications) and animal/human toxicity data, provide the data base for assessing potential risks associated with the use of a specific pesticide.

This document is organized in three sections and an Appendix. Section 1 (this section) presents the background for the study and the intended uses of the document. Section 2 identifies the sources of data and data acquisition and assessment methodology. Section 3 presents an overall summary of the collected data and results. Detailed data on the pesticides addressed are presented in the Appendix which consists of 18 subsections ("separate documents"), one for each pesticide reviewed. Each review document in the appendix consists of a summary and several sections which provide, where available, the following information for the specific pesticide reviewed: (a) background data on application method/rate, efficacy, extent of use, mode of action, etc.; (b) physical and chemical properties of the active ingredient; (c) environmental fate, including uptake, metabolism and persistence in plants (or in insects for the insecticides), degradation, volatilization and adsorption/leaching in soil, and chemical and biochemical alterations in the aqueous environment; (d) impacts on non-target plants and organisms including crops, fish and other aquatic organisms, wildlife and beneficial insects, and potential for bioaccumulation; and (e) references to all data sources used.

2.0 DATA SOURCES, METHODOLOGY AND REVIEW PROCEDURE

2.1 SELECTION OF SPECIFIC PESTICIDES

Table 1 lists the eighteen pesticides for which environmental fate and impact profiles are presented in the Appendix. These specific pesticides were selected from a much larger list of candidates based in part on discussions with technical experts most familiar with pest management problems and pesticide usage in the four major U.S. forest production regions covered in the Forest Use Chemicals Project*. Additional considerations in selecting the pesticides listed in Table 1 were: (1) the project funding and schedule constraints which limited the total number of pesticides which could be addressed; (2) representation of major pesticides used; and (3) inclusion of "problem/controversial" pesticides, newer pesticides with potential for future large-scale application, and biological pesticides which have often been promoted by environmentalists as viable substitutes for chemical pesticides.

2.2 DATA SOURCES AND DATA COLLECTION METHODOLOGY

The major sources of data used in developing pesticide fate and environmental impact profiles consisted of published literature; data provided by the Ecological Effects and Environmental Fate Branches of EPA's Office of Pesticide Programs, based on their review of the EPA's pesticide registration files; and discussions with technical experts at pesticide manufacturing companies, academic institutions, timber companies, U.S. Department of Agriculture, and State Forest Service agencies. The published literature was searched via computerized data bases such as Pollution Abstracts, TOXLINE, MEDLARS, NTIS, and DIALOG. These searches were updated via review of the more recent issues of pertinent periodicals such as Archives of Environmental Contamination and Toxicology, Agronomy Journal, Down to Earth, and Journal of Forestry.

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*The four production regions are: Northwest, Great Lakes, Northeast (Maine) and Southeast; these regions were chosen since they collectively account for close to 70 percent of the total commercial forest land in the U.S. and cover a spectrum of geographic/climatic conditions, species diversity and pest management problems.

TABLE 1. PESTICIDES ADDRESSED IN THE PROJECT

Common Name	Major Trade Names
Herbicides	
Amitrole	Amitrole T, Cytrol Amitrole-T, Weedazol
Atrazine	AAtrex 80W, 90W, 4L, 4CL
Dalapon	DOWPON, DOWPON M, DOWPON C, Radapon
Dicamba	Banvel
2,4-D	Weedone LV-4, Esteron 99 Concentrate, Weedar 64
Fosamine Ammonium	"Krenite"Brush Control Agent, Krenite S Brush Control Agent
Glyphosate	Roundup
Hexazinone	"Velpar" "Gridball" Brush Killer, "Velpar" Weed Killer, "Velpar" L Weed Killer
MSMA	Ansar, Bueno, Daconate
Picloram	Tordon, Amdon
Simazine	Princep
Triclopyr	Garlon 3A, Garlon 4
Insecticides	
Acephate	Orthene
Carbaryl	Sevin-4-Oil; Sevin 50WP, 80WP, 80S
Trichlorfon	Dylox 1.5 Oil, Dylox 4
Biologicals	
Bacillus thuringiensis	Dipel, Thuricide
Nucleopolyhedrosis virus	Gypcheck, TM-Biocontrol-1
Pheromones	(various)

The individuals/organizations who contributed to the data base for the study are too numerous for complete listing in this report. Table 2 provides a partial listing of those individuals who provided considerable unpublished data and/or copies of published reports and journal articles for use in the study. In connection with the Forest Use Chemicals Project, field trips were also undertaken to the four production systems for the purpose of collecting "real world" data. These trips, which were of several days duration each, were most helpful in developing appreciation for the region-specific pest management problems and provided an opportunity for face-to-face discussions with individuals most familiar with such problems.

2.3 DATA EVALUATION AND REVIEW PROCEDURE

The literature searches which were conducted identified a relatively large number of journal articles and published reports as potentially containing environmental fate and impact data for many of the pesticides of interest. These identified references and other reports and articles which were obtained from other sources were reviewed and those judged to be of unacceptable or questionable quality (e.g., due to inadequate documentation or assertions without providing supportive technical data) were screened out. Only those materials which, based on the data and discussions presented, could be judged to be of adequate technical quality were used in developing the environmental fate and impact profiles.

To assure accuracy and completeness and to give the pesticide registrants an opportunity to provide additional data not available to the study from other sources, the draft environmental fate and impact documents were forwarded to pesticide registrants and, in the case of biological pesticides, to technical experts for review and comment. Table 3 lists the pesticide registrants and technical experts to whom the draft documents were sent for review. A copy of the typical request letter accompanying the draft documents is reproduced as Table 4. Comments received from the reviewers were evaluated and incorporated, when appropriate, in the revised documents which appear in this report. In all cases, the reviewers' comments were very constructive and, in the case of certain newer pesticides such as hexazinone for which little data were available in the open literature, were substantial, thus requiring major revisions, substantial expansion, and hence significant improvement in the accuracy and completeness of the documents.

TABLE 2. KEY INDIVIDUALS/ORGANIZATIONS CONTRIBUTING TO THE DATA BASE FOR THE STUDY

Individual	Affiliation
Prof. Norm Akesson	- Agricultural Experiment Station, University of California, Davis, CA
Dr. Larry Atkins	- Dept. of Entomology, University of California, Riverside, CA
Mr. William Bedard	- USFS, Berkeley, CA
Dr. Morton Biskind	- Pharmocologist, Westport, CT
Mr. Temple Bowen	- Maine Bureau of Forestry, Augusta, ME
Mr. Perry Coy	- Pesticide Use Enforcement, State of California, Berkeley, CA
Dr. Don Dahlsten	- University of California (Div. of Biological Control), Albany, CA
Dr. Gary Daterman	- Pacific NW Forest and Range Experiment Station, U.S. Forest Service, Corvallis, OR
Mr. Richard Dunkel	- California Department of Food and Agriculture, Sacramento, CA
Mr. Richard Duvall	- California Department of Food and Agriculture, Sacramento, CA
Dr. L. C. Folmar	- National Marine Fisheries Service, Seattle, WA
Dr. Richard Garcia	- University of California (Div. of Biological Control), Albany, CA
Mr. Dean Gjerstad	- Department of Forestry, Auburn University, Auburn, AL
Mr. Dave Graham	- Forest Insect and Disease Management, Forest Service/USDA, Washington, D.C.
Dr. H. Gratkowski	- Pacific NW Forest and Range Experiment Station, U.S. Forest Service, Corvallis, OR
Dr. G. W. Green	- Canada Forestry Service, Forest Management Institute, Sault Ste. Marie, Ontario
Mr. Larry Gross	- U.S. Forest Service, Milwaukee, WI
Dr. Illo Gauditz	- Weyerhaeuser Co., Centralia, WA
Mr. Dan Hartman	- Consolidated Paper Company, Wisconsin Rapids, WI
Dr. Steve Herman	- Evergreen State College, Olympia, WA
Mr. Ralph Hodosh	- Conrel, Needham Heights, MA
Dr. E. F. Holling	- Institute of Animal Research Ecology, University of British Columbia, Vancouver, Canada
Mr. Fred Honning	- Forest Insect and Disease Management, Forest Service/USDA, Washington, D.C.
Dr. Allen Isensee	- Pesticide Degradation Laboratory, USDA, Bartlesville, MD
Dr. Carl Johnson	- Entomology Department, Washington State University, Pullman, WA

-Continued-

TABLE 2. (Continued)

Individual	Affiliation
Dr. Donald Kaufman	Pesticide Degradation Laboratory, USDA, Bartlesville, MD
Dr. Philip C. Kearney	Pesticide Degradation Laboratory, USDA, Bartlesville, MD
Mr. Peter Kinsbury	Forest Pest Management Institute, Sault Ste. Marie, Ontario, Canada
Mr. Robert Kirshner	National Forest Products Association, Washington, D.C.
Mr. Leroy Kline	Oregon Department of Forestry, Salem, OR
Dr. Terry Lavy	Department of Agronomy, Altheimer Laboratory, University of Arkansas, Fayetteville, AR
Dr. William Lawrence	Weyerhaeuser Co., Centralia, WA
Mr. Jay Maitlen	USDA, Yakima Agricultural Research Laboratory, Yakima, WA
Dr. Maxwell McCormack	School of Forest Resources, University of Maine, Orono, ME
Mr. William McCredie	National Forest Products Association, Washington, D.C.
Dr. Jerry Michael	Southern Forestry Experiment Station, Auburn, AL
Dr. Daniel Neary	Forest Service/USDA, Gainesville, FL
Dr. Michael Newton	School of Forestry, Oregon State University, Corvallis, OR
Dr. David Pimentel	Department of Entomology, Cornell University, Ithaca, NY
Dr. Steven Radosevich	Department of Botany, University of California, Davis, CA
Mr. Lou Seymour	Sandoz Inc., San Diego, CA
Dr. Kathy Sheehan	University of California (Div. of Biological Control), Albany, CA
Dr. Robert Spears	School of Public Health, University of California, Berkeley, CA
Mr. William A. Tuttle	Forest Service (USDA), Milwaukee, WI
Dr. John Walstad	Department of Forest Science, Oregon State University, Corvallis, OR
Dr. Charles Webb	International Paper Co., Bangor, ME
Dr. David Wood	Department of Entomology, University of California, Berkeley, CA
Dr. Ed Woolson	Pesticide Degradation Laboratory, USDA, Bartlesville, MD
Prof. Wesley Yates	Agricultural Experiment Station, University of California, Davis, CA
Mr. Noel Yoho	International Paper Co., Mobile, AL

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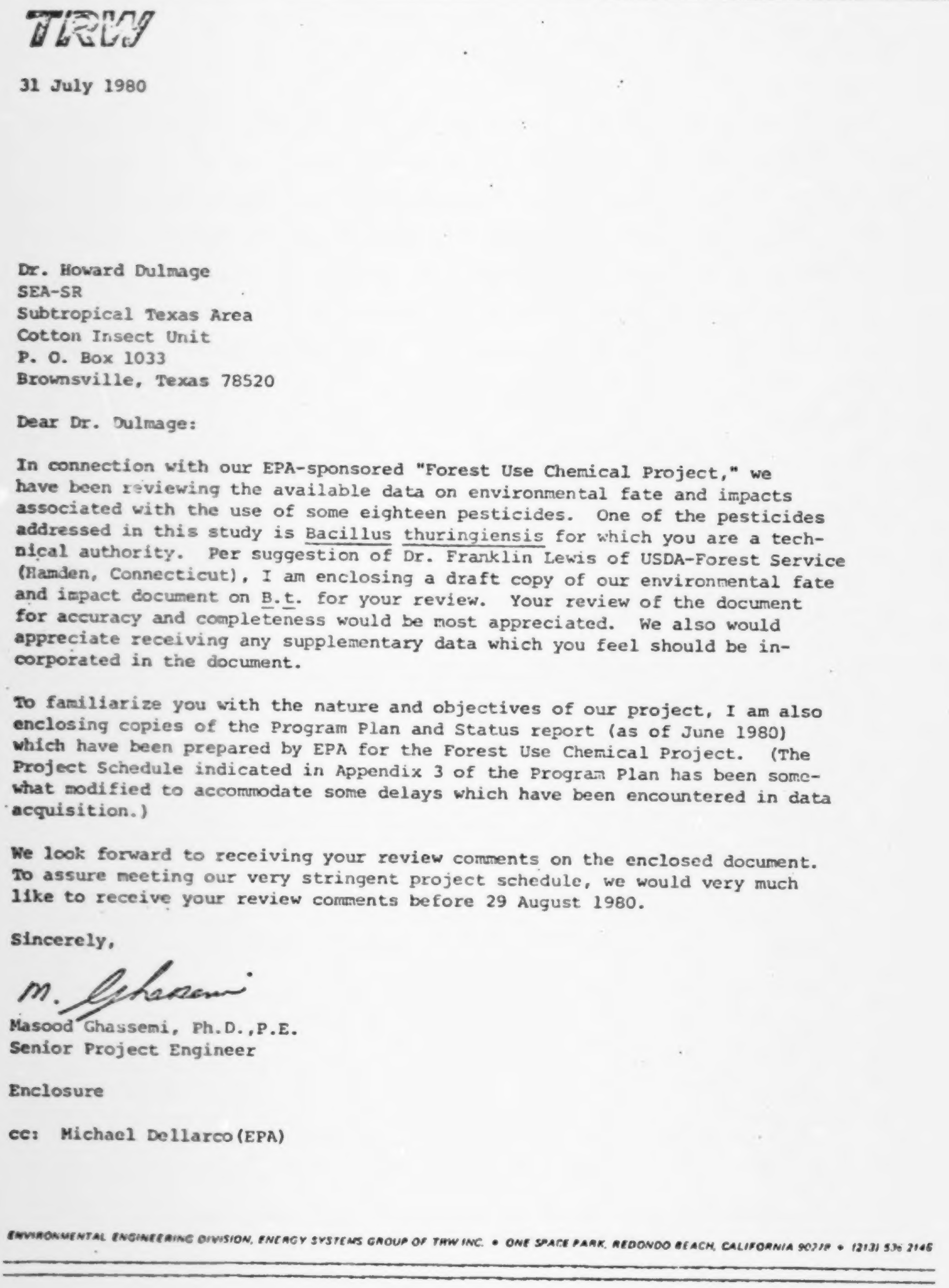
[*] The listing in this table does not include various divisions and branches of EPA's Office of Pesticides and Toxic Substances which made their data files available to the project, nor the pesticide registrants and other technical experts, listed in Table 3, who reviewed the draft documents and provided references and much supplementary information.

TABLE 3. PESTICIDE REGISTRANTS AND OTHER TECHNICAL EXPERTS WHO PROVIDED REVIEW COMMENTS ON THE DRAFT DOCUMENTS

Reviewers	Pesticides
Registrants	
Chevron Chemical Co.	Acephate
Ciba-Geigy Corp.	Atrazine, simazine
Diamond Shamrock	MSMA
Dow Chemical	Dalapon, picloram, 2,4-D, triclopyr
DuPont	Hexazinone, fosamine ammonium
Mobay Chemical Corp.	Trichlorfon
Monsanto	Glyphosate
Union Carbide	Carbaryl, amitrole
Velsicol	Dicamba
Other Technical Experts	
Dr. Robert Holst (EPA/OPTS-HED)	All 18 pesticides
Dr. Jack Plimmer (USDA)	Pheromones
Dr. H. T. Dulmage (USDA)	*Bacillus thuringiensis*
Dr. Franklin Lewis (USDA)	Nucleopolyhedrosis virus
Dr. Normand Dubois (USDA)	*Bacillus thuringiensis*

TABLE 4. TYPICAL REQUEST FOR REVIEW OF THE DRAFT DOCUMENTS



TRW

31 July 1980

Dr. Howard Dulmage
SEA-SR
Subtropical Texas Area
Cotton Insect Unit
P. O. Box 1033
Brownsville, Texas 78520

Dear Dr. Dulmage:

In connection with our EPA-sponsored "Forest Use Chemical Project," we have been reviewing the available data on environmental fate and impacts associated with the use of some eighteen pesticides. One of the pesticides addressed in this study is Bacillus thuringiensis for which you are a technical authority. Per suggestion of Dr. Franklin Lewis of USDA-Forest Service (Hamden, Connecticut), I am enclosing a draft copy of our environmental fate and impact document on B.t. for your review. Your review of the document for accuracy and completeness would be most appreciated. We also would appreciate receiving any supplementary data which you feel should be incorporated in the document.

To familiarize you with the nature and objectives of our project, I am also enclosing copies of the Program Plan and Status report (as of June 1980) which have been prepared by EPA for the Forest Use Chemical Project. (The Project Schedule indicated in Appendix 3 of the Program Plan has been somewhat modified to accommodate some delays which have been encountered in data acquisition.)

We look forward to receiving your review comments on the enclosed document. To assure meeting our very stringent project schedule, we would very much like to receive your review comments before 29 August 1980.

Sincerely,

M. Ghassemi

Masood Ghassemi, Ph.D.,P.E.
Senior Project Engineer

Enclosure

cc: Michael Dellarco(EPA)

ENVIRONMENTAL ENGINEERING DIVISION, ENERGY SYSTEMS GROUP OF TRW INC. • ONE SPACE PARK, REDONDO BEACH, CALIFORNIA 90278 • (213) 536 2146

3.0 OVERVIEW OF THE AVAILABLE DATA ON ENVIRONMENTAL FATE AND IMPACTS

The available data on environmental fate and impacts for the eighteen pesticides addressed in this study are presented in the Appendix and are summarized in Tables 5 through 9. Based on the data presented in the Appendix and in the summary tables, and on the discussions which were held with forestry organizations, timber companies and technical experts during the site visits to various forest production regions, the following are the highlights of the data and some general observations on the nature, significance, and limitations of the available data and some recommendations for future studies.

3.1 SCOPE AND LIMITATIONS OF THE DATA AND SOME GENERAL RECOMMENDATIONS

- Most of the available data have been generated by the pesticide registrants in support of pesticide registration for specific uses. Since only a few of the pesticides have the same registrant and are for the same applications, the data for different pesticides are not generally on the same bases (e.g., in terms of efficacy, non-target plants of interest, types of animals tested for toxicity or soils used in leaching and degradability studies, and experimental conditions used) and hence the comparison of various pesticides is often inappropriate or very difficult. Field studies in which efficacy and environmental persistence and impacts of pesticides are compared under similar application conditions can provide the "real world" data needed for comparative assessment of relative merits and shortcomings of pesticides recommended for the same applications. "Forestry cooperatives" such as those which have been recently established and are now operative in the South (Auburn University Forestry Chemicals Cooperative) and in Maine (Cooperate Forestry Research Unit, University of Maine) would be appropriate vehicles for carrying out such independent comparative studies.

- Most of the field studies of pesticide application in the past have emphasized assessment of efficacy, with collection of comprehensive environmental data being of only recent interest. Field evaluations in experimental plots, however, provide excellent "piggyback" opportunities for cost-effective collection of environmental data; such opportunities must be taken full advantage of in cooperative effort involving registrants, researchers in academic institutions, timber companies, and state and federal environmental regulatory agencies.

- A considerable portion of the available data has been obtained in conjunction with the agricultural uses of pesticides and hence not all such data would be applicable to forestry applications due to differences in soil characteristics, climate and sunlight conditions and application rates.

- While extensive data have been generated by the registrants through systematic and well-designed scientific studies for a few of the pesticides (particularly the newer herbicides), such comprehensive data bases do not exist for most of the pesticides addressed in the study. Many assertions in the literature as to "low" or "moderate" toxicity, mobility or persistence of certain pesticides appear to be unsubstantiated; where some quantitative data have been reported (e.g., TL_{50} values for toxicity to fish), there appears to be certain overlapping and inconsistencies in assigning qualitative descriptors based on quantitative data. For most pesticides, little data are reported on fate in the aqueous environment.

- In general, the majority of environmental fate data are from laboratory tests conducted under carefully controlled and simplistic conditions which do not necessarily reflect the very complex forest ecological systems.

- Laboratory animal toxicity data which have been reported for many of the pesticides by themselves do not provide indications of potential risk to aquatic and terrestrial life under actual forest use conditions. To estimate risks, toxicity data must be used in conjunction with data on actual exposure (populations exposed, concentration levels and persistence) in the forest environments. Data from actual monitoring of forest streams and wildlife food sources, and of populations and diversities of aquatic and terrestrial communities prior and subsequent to pesticide application are needed in developing the data base for risk assessment.

- Up-to-date detailed technical information on various aspects of pesticide use, such as the data presented in this document on fate and environmental impacts of pesticides, are not generally available to the practicing foresters and local and state agencies who are interested in the safe use of pesticides. Publication and distribution of "information transfer" documents such as this document, and sponsorship of technical workshops and seminars would be valuable vehicles for making the latest technical data and research and development results available to the user community.

3.2 HIGHLIGHTS OF THE REPORTED DATA

3.2.1 General Properties and Use Data (Table 5)

- Primary forestry application of the herbicides addressed in this study are for site preparation and conifer release; the insecticides (including biologicals) are used primarily for the control of spruce budworm, gypsy moth, tussock moth, and other forest insects.

- Aerial broadcast is by far the most prevalent application method for pesticides; the rate of application varies with the specific pesticide and use, and is generally less than 4 lb a.i. per acre.

TABLE 5. SUMMARY OF GENERAL PROPERTIES AND USE DATA

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
I. HERBICIDES							
Amitrole	Amitrol-T, Cytrol Amitrole-T, Weedazol	Union Carbide	Used on salmonberry and elderberry for site preparation and conifer release	Applied as a foliar spray at the rate of 2 lb a.i. per acre	Primarily in the coast range of the Pacific Northwest	Highly soluble in water (28 g/100g at 25 °C), and in polar solvents. Low volatility	—
Atrazine	AAtrex (80W, 90W, 4L, 4CL)	Ciba-Geigy	Conifer release, nursery applications of fir transplants, and seed orchards/production areas	Aerial broadcast or ground spot applications at 3 to 5 lb of 80% a.i./acre for conifer release; 2 lb a.i./acre in nursery applications; 2 – 4 lb a.i./acre in seed orchards/production	Primarily in the Pacific Northwest	Solubility 70 ppm in water. Low volatility (1.4 x 10^{-6} mm Hg at 30 °C)	Sometimes used in combination with dalapon for control of broadleaf weeds and grass for Douglas fir release in the Pacific Northwest; and with simazine in the South
Dalapon	DOWPON, DOWPON M, DOWPON C, Radapon	Dow	Site preparation, release, in seed orchard/production areas, and vegetation control in established plantings	3 to 15 lb/acre (DOWPON M) via ground or aerial spray	Used in Pacific Northwest (e.g., 14,354 lb applied to 2,900 acres in BLM Region 5 in (1976 – 1979). Data unavailable on usage in other regions	Very soluble in water; solubility of DOWPON M 110g/100 ml at 22 °C, in water containing 100 ppm hardness	Has been used in combination with atrazine and 2,4-D for control of broadleaf weeds
Dicamba	Banvel. Formulated as a water soluble salt, oil-soluble liquid, water-soluble liquid, emulsifiable concentrate. Often combined with 2,4-D	Velsicol Chemical Corp.	Primarily for site preparation to control deciduous shrubs and trees, certain conifers and forbs	Dimethylamine salt used undiluted (4 lbs acid equivalent per gal) or diluted 1:4 in water for cut surface injection	Used in southeastern pine forests and in the Pacific Northwest. Data do not indicate extensive use	Soluble in most organic solvents, poorly soluble in water (0.45 g/100 ml at 25 °C). DMA salt highly soluble in water (72 g/100 ml). Vapor pressure 3.4 x 10^{-5} mm Hg at 25 °C	—

(Continued)

TABLE 5. (Continued)

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
2,4-D	Weedone LV-4, Esteron 99 Concentrate, Weedar 64, Verton 2-D, DMA-4	Dow Chemical Company	Used as a selective broadleaf weedkiller for site preparation	Applied as foliage sprays by handgun or backpack mist blower, aerial application or ground rig applicators; applied at 2 to 4 lb acid equivalent of active ingredient per acre	Primarily in the Pacific Northwest and Great Lakes	Varies, depending on formulation. Water solubility of 2,4-D acid is 0.09g/100g at 25 °C; vapor pressure is 0.4 mm Hg at 160 °C. Water solubility of 2,4-D amine is 300g/ 100g at 20 °C. Butoxyethanol ester of 2,4-D insoluble in water; vapor pressure 4.5×10^{-6} mm Hg at 25 °C	—
Fosamine Ammonium	"Krenite" brush control agent; "Krenite" S brush control agent	Du Pont	Site preparation and conifer release	Aerial broadcast (3 to 12 lb a.i./acre for site preparation, less for release). Limited ground application	Primarily in the Pacific Northwest. Limited application in the South; used in experimental plots in the Northeast. Quantitative usage data unavailable	Highly water soluble (179g/100g). Low volatility (vapor pressure 4×10^{-6} mm Hg at 25 °C)	Relatively new herbicide (introduced in 1974). Most effective when applied in late summer or early fall and does not show its effects until the following spring.
Glyphosate	Roundup	Monsanto	Site preparation and release; seed orchards/ production areas, preplant nursery uses	Ground and aerial application; 1 to 1.5 and 3 to 4 qts per 10 gallon solution/acre for release and site preparation, respectively	Primarily in Pacific Northwest (1979, 4,100 lb in USFS Regions 5 and 6; 3,000 to 5,000 acres of state-owned forests treated annually); also, major uses by private timber companies. Limited use in the Northeast (1979, 6,000 lb used in Maine)	Solubility 1.2 percent in water at 25 °C; negligible vapor pressure	Relatively new herbicide (introduced in 1971). Primary uses are in agriculture and industrial/recreational areas

(Continued)

TABLE 5. (Continued)

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
Hexazinone	"Velpar" "Gridball" Brush Killer, "Velpar" Weed Killer, "Velpar" L Weed Killer; "Gridball" pellets available as 10% to 20% ingredient	Du Pont	Site preparation and pine release	Dependent on soil type, 5 to 10 and 7 to 20 lb/acre "Gridball" for release and site preparation, respectively; "Gridball" pellets applied by hand or with special aerial equipment. Rain necessary for solubilization of pellets and movement of hexazinone into soil	To date, primarily in the South (1979 estimated acreage treated: 6,500 acres)	Water solubility: 3.3g/ 100g at 25 °C; vapor pressure: 2×10^{-7} mm Hg at 25 °C; slowly decomposes in water	Very new herbicide; under evaluation in large-scale commercial applications in the South, Northwest and upper Midwest as possible substitute for 2,4,5-T
MSMA	Ansar, Bueno, Daconate, Weed-Hoe, Valson	Diamond Shamrock, Vineland Chemical	Site preparation and precommercial thinning	Applied by injection or cut surface of tree trunk	Approximately 5 metric tons/year used primarily in the Pacific Northwest	Soluble in water, non-volatile, forms insoluble salts with divalent cations	No photodegradation reported
Picloram	Tordon (101, 101R, 10K pellets, K) for forestry use; Tordon (2K, 22K, 202 Mixture, 225E Mixture, RTh) for non-forestry use; Andon	Dow	Site preparation and conifer release; occasional use in precommercial thinning	Spray solutions (2 oz to 3 lb/acre); pellets (2 to 8 lb/acre); stem injection (1 ml/ injection of Tordon 101)	Primarily in the South (in 1979, 51,500 acres, site preparation; 78,510 acres, release). Also used in Pacific Northwest and Great Lakes in smaller quantities	Picloram only slightly soluble in water (430 mg/ℓ), but potassium and amine salts highly water soluble. Vapor pressure 6.2×10^{-7} mm Hg at 35 °C; slightly higher for picloram esters	Also effective when used in combination with triclopyr and 2,4-D for control of mixed hardwood brush

(Continued)

TABLE 5. (Continued)

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
Simazine	Princep	Ciba-Geigy	Site preparation, conifer release, nursery applications	3 to 4 lb a.i. in 10 gal water/acre for site preparation and conifer release; 1.6 to 3.8 lb a.i. in 10 to 25 gal water/acre for nursery applications. Aerial broadcast and ground spot methods used	Used primarily in Pacific Northwest and to a limited extent in the South. Quantitative use data unavailable	Low volatility; vapor pressure 6.1 x 10^{-9} mm Hg at 20 °C. Slightly water soluble (3.5 ppmw at 20 °C)	Also used in combination with atrazine in both PNW and South
Triclopyr	Garlon 3A Garlon 4	Dow	Site preparation; conifer release	2 to 3 gal/acre (Garlon 3A) by broadcast application via low volume ground spray equipment or helicopter; 1/2 to one gal/100 gal water for high volume, full spray; also by tree injection	Used on experimental basis in Pacific Northwest, Northeast and South (1979, 100 acres in Washington, Oregon, California)	Solubility, 4.3g/100 mℓ in water; vapor pressure 1.3 x 10^{-6} mm Hg at 25 °C	Very new herbicide only recently registered for use in forestry. Most current experimental uses in PNW in ground applications for stump treatment and tree injection
II. INSECTICIDES							
Acephate	Orthene	Chevron Chemical Company (Ortho Division)	Used in seed orchards to control cone and seed insects; used in forests for control of spruce budworm and gypsy moth	In seed orchards, applied with ground spray rigs at 2/3 lb/ 100 gal water/acre. Aerially applied in forests at a rate of 2/3 to 1 1/3 lb in 1 gal/acre	Has been used to a limited extent against spruce budworms in Maine	Highly soluble in water (65%) and in polar organic solvents. Low vapor pressure (2 x 10^{-6} mm Hg at 25 °C)	Does not appear to photodegrade on surfaces or in water

(Continued)

TABLE 5. (Continued)

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
Carbaryl	Sevin-4-oil Sevin 50 WP, 80 WP, 80S	Union Carbide	Control of insects such as spruce budworm, gypsy and tussock moths	Aerial application (1 – 2 lbs a.i./acre Sevin-4-oil or Sevin 80S); ground application (2 lb a.i./acre Sevin 80S with mist-blower; one lb a.i./acre Sevin 80S with hydraulic sprayer)	Primarily in Northeast (8.2 and 2.5 million acres in Maine in 1975 – 79 and 1979, respectively, for spruce budworm control; in 1979 42,000 acres in Northeast for gypsy moth control). Also used in Pacific Northwest for Douglas fir tussock moth and in Rocky Mountain states for Western spruce budworm; quantitative usage data unavailable	Slightly water soluble (40 ppm at 30 °C). Low volatility (0.002 mm Hg at 40 °C)	Widely used to control insect pests on field crops, gardens and rangelands
Trichlorfon	Dylox 1.5 oil Dylox 4	Mobay Chemical Corp	Control of gypsy moth, spruce budworm, forest tent caterpillars	Applied at 1 lb a.i. per acre. Aerial application	Registered for use in Maine and New Hampshire for gypsy moth and spruce budworm; in Louisiana and Alabama for forest tent caterpillars. 97,000 acres treated in Maine in 1979	Solubility in water 12.3g/100g. Slightly soluble in paraffinic hydrocarbons. Vapor pressure 7.8 x 10^{-6} mm Hg at 20 °C. Stable in acid, rapidly hydrolyzed in alkaline solutions	—
III. BIOLOGICALS							
Bacillus thuringiensis	Dipel, Thuricide	Abbott Laboratories Sandoz Inc.	For control of spruce budworm, gypsy moth, Douglas fir tussock moth, forest tent caterpillars, spring and fall cankerworms	Aerial application of 1.8 to 8 BIU/acre, depending on target insect	Most extensive use is for control of spruce budworm in Maine on about 200,000 acres/ year	Active ingredient consists of spores and parasporal crystals of the bacterium, approx. 1μ in diameter	Photodegradation half-life of 0.3 to 3 days on exposed leaves

(Continued)

TABLE 5. (Continued)

Pesticide Common Name	Major Trade Names/ Formulations	Major Registrant	Forestry Applications	Application Rate and Method	Extent of Use	Relevant Physical/ Chemical Properties of Active Ingredient	Miscellaneous
Nucleopolyhedrosis virus	Gypcheck, TM-Biocontrol-1 Elcar (for agricultural use)	USDA, Sandoz Inc.	For control of gypsy moth, Douglas fir tussock moth. Elcar for control of cotton budworm and tobacco budworm	Applied at 25 – 125 million units/acre for gypsy moth; 1 billion units/acre for tussock moth. Aerial application.	Limited	Active ingredient consists of polyhedra, approx.1μ in diameter	Inactivated by sunlight on surfaces in 3 – 15 days
Pheromones	Pheromones are specific for a particular insect. Some trade names are Chek/Mate, Pherocon EPSM, Pherocon GM	Hercon, Conrel, Zoecon	Current uses primarily for biosurveys and monitoring of forest insect pests. Limited use for mating disruption or mass trapping	Applied at rates approximating those levels which are naturally present. Applied as flakes, luretape, rubber caps or wicks, hollow plastic capillaries	Used against gypsy moth, elm bark beetle, pine shoot moth, elm bark beetle, spruce budworm, Western pine shoot borer. Much use is still experimental	Volatile organic compounds highly selective for a single species; formulated to closely represent the natural insect pheromone	—

- The ban on forestry use of 2,4,5-T has been a major impetus for the recent and current evaluation of several new herbicides (e.g., hexazinone and glyphosate) and testing of some older herbicides (e.g., picloram) in forestry applications. Because of the limited supplies, some of the newer herbicides (e.g., triclopyr) have only been tested on small experimental plots. Some of the biological pesticides (specifically pheromones) have also been used only on a small scale experimental basis.

- Some pesticides are more widely used in specific regions than in others (e.g., use of amitrole in the Pacific Northwest) and for specific pests (e.g., use of specific pheromones for specific insects or use of carbaryl for spruce budworm and gypsy and tussock moths).

- While some data on quantitative usage of pesticides by the public sector are available, very little data are publicly available on such uses by the private sector.

- At the present time, most herbicide usage is in the Northwest whereas large scale insecticide use is primarily in the Northeast. Insecticide use in the Northeast and in other regions is carried out only during pest outbreaks.

- Certain herbicides are used in combinations to improve efficacy (e.g., use of atrazine in combination with dalapon, 2,4-D, or simazine).

- With few exceptions (e.g., dalapon and amitrole), herbicides are only slightly soluble in water and have low vapor pressures; these properties have important implications in determining fate in water and soil.

3.2.2 Uptake and Metabolism in Plants/Insects (Table 6)

- The uptake of herbicides by plants is primarily via roots and/or foliage. Insecticides are taken up by insects through contact with aerosol sprays and/or ingestion of contaminated foliage. Additives are often used with certain herbicides (e.g., fosamine ammonium) to promote plant penetration and uptake.

- The mechanisms of action for certain pesticides (e.g., glyphosate and picloram) are not fully known. In general, the modes of action of herbicides include interference with the photosynthesis process, metabolism and various growth responses in plants. All three chemical insecticides are nerve poisons and exert their action by inhibiting acetylcholinesterase in insects. *Bacillus thuringiensis* and nucleopolyhedrosis virus are insect pathogens whereas pheromones are behavior modifying agents (e.g., disrupt mating).

- Not all herbicides are metabolized in plants; for those which are, the mechanism of degradation is either unknown or varies and includes conjugation, hydrolysis, and ring and side chain cleavage.

TABLE 6. SUMMARY OF DATA ON UPTAKE AND METABOLISM IN PLANTS (OR INSECTS)

Pesticide	Mode of Uptake	Mode of Action	Metabolism
I. HERBICIDES			
Amitrole	Absorbed through leaves and roots; readily translocated.	Prevents chloroplast development in new growth.	Conjugates formed in plants. One breakdown product is 3 ATAL, which is less toxic than amitrole.
Atrazine	Roots and leaves (minor). Foliar uptake enhanced by addition of adjuvents such as mineral oil. Some accumulation in marginal zone of leaves.	Inhibits photosynthesis resulting in defoliation and plant death.	Four principal degradation mechanisms: (1) hydrolysis to hydroxy atrazine; (2) conjugation with glutathione or amino acids at 2-position of triazine ring; (3) N-dealkylation of side chain group; (4) s-triazine ring cleavage.
Dalapon	Roots and foliage. Rapidly translocates throughout the plant and accumulates in areas of high metabolic activity (vegetative buds and fruiting areas).	Causes leaf chlorosis and abnormal growth responses typical of growth regulators; also displays acute contact toxicity.	Not metabolized within 2 weeks following uptake; metabolism beyond 2 weeks not demonstrated.
Dicamba	Absorbed by roots or foliar tissues; readily translocated.	An effective plant growth regulator which alters root and shoot development and causes leaf malformation, increased branching, petiole and stem curvature and abnormal flowering.	Species dependent; may involve ring hydroxylation, formation of conjugates, demethoxylation. Half-life of about two weeks observed for the amine salt in grasses.
2,4-D	Absorbed through leaves, stems, or roots; readily translocated.	Acts as an analog of the growth hormone, indole-2-acetic acid, to cause loss of normal growth. Some tissues are stimulated while others are inhibited in their development.	May include side chain degradation or lengthening, ring hydroxylation or cleavage, conjugation, metabolite formation. High residue levels not expected.

Continued)

TABLE 6. (Continued)

Pesticide	Mode of Uptake	Mode of Action	Metabolism
Fosamine Ammonium	Absorbed by foliage, buds, and stems; uptake facilitated by addition of surfactants.	**Interferes with spring bud development; produces miniature spindly chlorotic leaves which do not photosynthesize adequately.**	**Half-lives of 2-3 weeks in apple seedling leaves and 7 days in pasture flora.** Metabolites were carbamoyl phosphoric acid (CPA) and carboxyphosphonic acid, which reached maximum concentration after 2 weeks. No residue found in pasture turf twelve months after application.
Glyphosate	Primarily through foliage; some root uptake, depending on soil type. Foliage uptake growth enhanced by humidity and surfactants.	Not fully understood; may involve blockage of aromatic amino acid biosynthesis.	**No significant degradation in plants up to 20 days after treatment (long term data unavailable).**
Hexazinone	Root (pellets) root and foliar (foliar) spray).	Interference with photosynthesis process resulting in defoliation and plant death.	Metabolized in plants, with very low residue levels after several months; a number of degradation products identified.
MSMA	Uptake by roots and leaves.	May interfere with plant phosphorous metabolism; causes chlorosis.	**Data on cotton indicate little metabolism; metabolized to organic arsenicals in sensitive plants. Found at levels of 116 ppm arsenic in pine needles several months after application.**
Picloram	Roots (spray pellets); foliage (spray)-less rapid uptake than by root; rapidly translocated throughout the plant, with tendency for accumulation in new growth.	**Growth regulator; exact mechanism not known.**	Relatively stable and remains largely intact within the plant; small amounts degrade via decarboxylation, conjugate formation with proteins and other mechanisms.

(Continued)

TABLE 6. (Continued)

Pesticide	Mode of Uptake	Mode of Action	Metabolism
Simazine	Roots; limited foliar uptake when used with surfactants or when leaves are physically damaged (e.g., due to hail).	Inhibits photosynthesis by arresting Hill reaction in chloroplasts.	Readily metabolized via 4 major mechanisms: hydrolysis; N-dealkylation of side chains; conjugation with amino acids; and s-triazine ring cleaveage.
Triclopyr	Roots and leaves. Readily translocated throughout the plant. Application to leaves results in accumulation in shoots.	Induces auxin-type responses; affects longitudinal cell structure and prohibits bending of stalks and stems in phototropic response.	Data unavailable on metabolic degradation (if any).
II. INSECTICIDES			
Acephate	Penetrates plant tissues within 24 hours. Kills insects on contact or upon ingestion of treated plants.	Neurotoxic to insects; inhibits acetycholinesterase.	Metabolized in plants to methamidophos, O,S-dimethylphosphorothioate, S-methyl acetylphosphoroamidothioate and unidentified products.
Carbaryl	By exposure to direct application; or by ingestion of contaminated foliage (insects, animals) or root uptake (plants).	Nerve poison; inhibits acetylcholinesterase.	Readily metabolized by insects to l-naphthol and N-methylcarbamic acid, which further decompose. Metabolized by animals to l-naphthol and numerous other hydrolysis, hydroxylation and epoxidation reactions. Metabolized by plants to products via oxidation, hydrolysis, hyroxylation and conjugate formation.

(Continued)

TABLE 6. (Continued)

Pesticide	Mode of Uptake	Mode of Action	Metabolism
Trichlorfon	Kills insects on contact or by stomach action upon ingestion. Available data suggests limited uptake by plants.	An organophosphate; inhibits acetylcholinesterase in insects and other organisms.	Several metabolites in plants, but only DDVP is toxic. Two main degradation pathways in animals: hydrolysis and dehydrochlorination; DDVP is formed, hydrolyzed and excreted.
III. BIOLOGICALS			
Bacillus thuringiensis	No evidence for uptake in plants. Ingested by insects.	Bacterial toxin attacks midgut epithelium of insects; bacteria cause septicemia in insects.	None in plants. Toxin is activated in the insect gut (requires pH 9.0 to 10.5 and gut enzymes). Bacteria reproduce in insect tissues.
Nucleopolyhedrosis virus	No evidence for uptake in plants. Ingested by insects.	Virus infects susceptible insects.	None in plants. Virus is propagated in living host larvae; infectious polyhedra are formed.
Pheromones	No uptake occurs.	Disrupts natural insect behavior e.g., mating or aggregation.	Not metabolized.

Trichlorfon and carbaryl are metabolized by insects to various degradates; all three chemical insecticides are also metabolized in plants.

- Rates of metabolism have not been established for all pesticides, but are expected to vary with the pesticide and application conditions. Half-life values of 2 weeks for dicamba in grasses and 2-3 weeks and 7 days for fosamine ammonium in apple seedling leaves and pasture flora, respectively, have been reported. Levels of residue in plants which are reported for only a few herbicides (e.g., hexazinone, fosamine ammonium, and 2,4-D) indicate low levels several months after application.

3.2.3 Fate in Soil (Table 7)

- Processes which impact the fate of the pesticides in soil are adsorption/leaching-runoff, chemical and microbial degradation, photodegradation and volatilization. The extent that each of these processes impact the persistence of a pesticide in the soil environment is dictated by the physical (particularly water solubility and vapor pressure) and chemical properties of the pesticides, soil characteristics (particularly organic content and pH) and climatic conditions (e.g., rainfall and temperature). Microbial degradation - and not chemical hydrolysis, volatilization, or photodegradation - is by far the major route for dissipation of pesticides from soils.

- Actual field data on the persistence of pesticides (residue levels and half-life values) in the forest soil have only been reported for a few pesticides, most notably hexazinone, 2,4-D, and simazine.

- Reported degradation data indicate that, depending on the soil conditions, half-life of pesticides may be very low (e.g., less than one day for acephate) but is generally in the order of several months; arsonates which are degradation products of MSMA have a half-life in soil of about 6 years. Actual residue data under actual conditions of use in forestry are available for only selected pesticides.

- Mobility in soil is inversely related to a pesticide's affinity for adsorption to and/or chemical reaction with soil particles. In general, pesticides/formulations with low water solubility (e.g., atrazine and simazine) and pesticides which have strong chemical affinity for soil particles (e.g., fosamine ammonium and glyphosate) are relatively immobile and are not readily leached (or leached to great depths) in the soils. In general, adsorption is greater (mobility is lower) in soils containing higher organic content and at lower pH levels and temperatures.

- In general, some loss of pesticides in runoff is likely if heavy rainfall occurs soon after application. Actual monitoring of residue levels in forest streams subsequent to pesticide application

TABLE 7. SUMMARY OF DATA ON FATE IN SOIL

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
I. HERBICIDES			
Amitrole	Reversibly adsorbed to soil; adsorption greater in high organic soils, and at lower pH. Leaching occurs in sandy soils, but greatly reduced in clay soils.	Degradation is chemical and microbial; depends on soil moisture, temperature, pH. Detectable residue persists from several days to 6 months or more.	Volatilization expected to be limited due to amitrole's low volatility. Amitrole appears stable under UV light.
Atrazine	A low mobility herbicide. Readily and reversibly adsorbed on soil. Adsorption stronger on soils with high organic matter, lower pH, moisture and at lower temperature. Leaching confined to upper 6 in. of soil in many soil types. Significant loss in runoff (5-10%) may occur if heavy rainfall occurs soon after application.	May remain at phytotoxic levels for over one year depending on soil type and climate conditions. Degrades via chemical and microbial routes. Principal chemical degradation route is hydrolysis to hydroxy atrazine, (half-life 66 days at pH 3, 81 days at pH 11). Microbial degradation occurs via dealkylation, ring cleavage and hydroxylation of 2-chloro group. Nitrosoatrazines (suspected carcinogens) not formed in significant amounts when atrazine (2 ppm in 7,5 cm of soil or 2 lb/acre) applied with ammonium nitrate fertilizer (100 ppm).	Photodegrades if prolonged sunlight and high temperature follow application, but precede precipitation (47 and 60% losses observed after exposure to spring sunlight in agricultural fields 25 and 60 days, respectively). Mechanism and products of photodegradation unknown. Volatilization, if any, would occur 1 to 2 days after application.
Dalapon	Limited adsorption to soil in laboratory studies; however, little leaching observed beyond upper 6 in. of soil under field conditions due to rapid microbial degradation. Quantitative data on runoff rates unavailable.	Microbial degradation major route of dissipation from soil; chemical hydrolysis minor to negligible. Rate of microbial degradation dependent on soil type, temperature, pH, moisture content and application rate. Generally persists between 2 weeks and several months at pH>5.	Volatilization considered insignificant under field conditions. Photodegradation considered unlikely due to poor absorption of light.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
Dicamba	Considered to be a very mobile herbicide; mobility greater at higher pH. Does not readily adsorb to soil but can adsorb to clays. Readily leached from soils; runoff possible with heavy rainfall after spraying. No dicamba residues detected in streams after 11 days following forest application of 1.12 kg/ha in 37.8 liters of water.	Degradation is primarily microbial; extent depends on soil conditions. Breakdown product is 3,6-DCSA. Generally does not persist more than several months in most soils.	Photodecomposition not expected to be significant. Vapors from soil-incorporated dimethylamine salt shown to be phytotoxic to beans.
2,4-D	Adsorbs more strongly to soils with higher organic matter; does not adsorb strongly to clay. Leaching generally depends on the formulation, soil properties, and amount of rainfall; polar salts leach more readily than esters. Potential for runoff is greater for esters which do not leach so readily.	Degradation depends on soil temperature, moisture, organic matter content of soil; it is primarily microbial. Under field conditions, 2,4-D esters normally hydrolyze to the acid within a few days. Only 6 percent remained in forest floor material 35 days after application of 2.24 and 4.48 kg/ha of 2,4-D.	Volatilization depends on vapor pressure-acids, salts, amines are less volatile than esters; greater in soils with low organic matter and clay content.
Fosamine Ammonium	A low mobility herbicide. Strongly adsorbed to and not readily leachable in soils high in clay and heavy metals content. Remained in top 12 inches of Fallsington soil under simulated rainfall conditions. Loss in surface runoff possible especially after heavy rainfall soon after application.	Half-life of one week observed under field conditions in Florida, Delaware and Illinois at practical application rate of 11.3 kg/hr. No residues detectable after 3 – 6 months. Half-life of 10 days determined in laboratory study. Undergoes chemical hydrolysis in soil to carbamoylphosphonic acid. Is decomposed rapidly by soil microorganisms.	No data available on photodegradation rates. Has low volatility.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
Glyphosate	Strongly adsorbed to soil via phosphoric acid functional group. Adsorption highest in soils with high organic content; minimal in sand. Also binds readily to kaolinite, illite and bentonite clays. Minimal mobility via leaching and runoff. No leachate after elution through soil columns for 45 days.	Decomposed rapidly by soil microorganisms under aerobic and anaerobic conditions. Principal soil metabolite is amino methylphosphonic acid. No appreciable chemical degradation.	Volatilization negligible due to low vapor pressure. Does not photodegrade under laboratory conditions; photodegradation in the field considered negligible.
Hexazinone	Hexazinone and at least some of its degradation products wash into the soil with rainwater; classified as "very mobile", with mobility dependent on soil type. In a forest watershed study (application rate 16.8 kg/hr), a series of 19 storms produced a residue loss of 0.5% of the applied hexazinone.	Degrades by soil microorganisms. Half-life could be as short as 1 month but up to about 6 months, primarily depending on soil type and conditions. Several triazine compounds identified as degradation products.	Will photodegrade on soil surface; based on laboratory tests, photodegradation half-life estimated at 37 days.
MSMA	Converted to arsenate in soil which is tightly bound; little leaching. No residues detected in forest streams after injection of MSMA for precommercial thinning; detection limit was 0.01 ppm.	Converted to a number of organic and inorganic arsenic compounds; degradation largely microbial. Degradation products are largely arsonates which have a half-life in soil of about 6 years.	None reported.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
Picloram	Mobility a function of soil type, pH, application rate and rainfall. Adsorption greatest in soils high in organic matter. Seldom leaches below 20 to 30 cm for most soil types except sandy soil. Did not leach below the upper inches of soil in a forest floor; runoff likely if heavy rainfall occurs within 1 to 2 months after application.	Reported half-lives varying from one to over 13 months; rate dependent on soil type and climatic conditions. Degradation occurs via microbial and not chemical routes. Decomposition rate increased under conditions favoring microbial growth (i.e., adequate moisture, temperature, etc). Microbial degradation thought to involve decarboxylation and ring cleavage.	Photodecomposes on soil surfaces, particularly under intense sunlight. Salt forms less subject to photodecomposition than ester forms. Photodegradation may involve pyridine ring cleavage.
Simazine	Low mobility; strongly adsorbed on soils high in organic content and in clay soils at low pH. In laboratory studies leached to depths of one to two inches in high organic muck soil; up to 6 inches in other soils with one inch applied water. Runoff potential high after heavy rainfall soon after application.	Half-life 4 to 6 months depending on soil type and climatic conditions. Less persistent in soils high in organic matter content. Residues of less than 1 ppm observed in Wolcott, CT forest plot 6 months after application of 4, 8, 12 and 16 lb/acre. Degrades via both chemical and microbial routes. Chemical degradation occurs via hydrolysis to hydroxy simazine; rate is pH dependent. Hydrolysis promoted by Fe and Al ions in soils. N-dealkylation primary mechanism of microbial degradation; hydroxylation and ring cleavage minor mechanisms.	Photodegradation insignificant under normal climatic conditions. Volatilizes only slightly, particularly in drier soils.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
Triclopyr	Classified a mobile herbicide with mobility dependent on soil type. Adsorption greater in soils with high organic content. Principal degradation product, trichloropyridinol, has low to intermediate mobility. In loam sand, 75 to 80% of applied triclopyr leached through 12 inch soil column after 15 days and 7.5 inches applied water. Trichloropyridinol less leachable (13 inches applied water required for complete passage through column). Residues of 6 ppb and 1 ppb in runoff found 5 and 9 months, respectively, after application of 3 lb/acre triclopyr as TEA salt and 150 cm rainfall.	Decomposed by soil microorganisms to 3,5,6-trichloro-2-pyridinol and trichloromethoxypyridine. Half-life (average 46 days) dependent on soil type and climatic conditions. Half-life of degradation to trichloro-2-pyridinol 79 to 156 days at 15°C, <50 days at25 to 35°C. Degrades 5 to 8 times slower under anaerobic than aerobic conditions at 25°C in silt loam soils. Does not degrade via hydrolysis or other chemical routes.	Some photodegradation possible from soil or foliar surfaces. Losses from volatilization considered insignificant due to low vapor pressure.
II. INSECTICIDES			
Acephate	Readily leached in soil; not strongly adsorbed.	Degradation is microbial; half-life reported to range from 0.5 to 13 days. The metabolite, Monitor, is also degraded with a reported half-life of 2 to 6 days.	No photodegradation reported. Volatility expected to be low.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching, and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.
Carbaryl	Adsorbed readily by organic soils but moves rapidly through inorganic soil. Adsorption completely reversible, due to weak chemical bonding. In soil leaching study, 72% retained in upper 20 cm of 100 cm organic soil column; none detected below 60 cm; only 50% retained in 100 cm inorganic soil column. Of 8.8 lb applied to field test plot, total of 0.14% lost in runoff of which 90% lost after heavy rainfall soon after application; concentration in runoff less than 0.1 ppb after 70 days.	Degradation primarily via microbial rather than chemical routes. Decomposed by bacteria and fungi to l-naphthol, several hydroxylated products and CO_2. Rate dependent upon soil type, temperature and type of microorganism. Chemical hydrolysis minor degradation route.	Expected to photodegrade on soil surfaces; photodegradation expected to be insignificant in the forest system; no quantitive data available on rates.
Trichlorfon	Reversibly adsorbed on soil; greatest adsorption in high organic soils. Subject to leaching due to its high water solubility.	Half-life in soil generally <30 days. Degrades more rapidly in alkaline soils. Degradation is microbial or chemical.	Thought to be minimal due to low volatility, high leachability.

(Continued)

TABLE 7. (Continued)

Pesticide	Adsorption, Leaching and Runoff	Chemical and Microbial Degradation	Photodegradation, Volatilization, etc.	Miscellaneous
III. BIOLOGICALS				
Bacillus thuringiensis	No data available	No data available	Inactivated by sunlight on most soils; inactivation more rapid under moist conditions.	Endospores may persist in soil for years.
Nucleopolyhedrosis virus	No data available	No data available	Inactivated by UV light.	Viral particles can persist in soil for years.
Pheromones	Data for oriental fruit fly pheromone indicates no leaching.	Half-life of pheromones in soil less than one day. Chemical hydrolysis possible. Many application materials (for e.g., fibers) are completely biodegradable.	Highly volatile; not expected to persist in soil.	—

have been reported for only some of the pesticides (e.g., hexazinone, dicamba, and MSMA).

- Because of their low vapor pressures, pesticide losses via volatilization are expected to be minimal. Only a few pesticides (e.g., atrazine, picloram, triclopyr, Bacillus thuringiensis, nucleopolyhedrosis viruses) would undergo photodegradation/photoinactivation on the soil surface; photodegradation/photoinactivation is expected to be insignificant in the forest system because of the lack of intense sunlight and extended exposure.

3.2.4 Fate in Water (Table 8)

- Dilution, adsorption on bottom sediments, chemical breakdown, microbial degradation, volatilization and photodegradation are mechanisms for dissipation of pesticides in the aqueous environment, with microbial degradation being by far the most prevalent degradation route. pH and temperature of the water are the two most important factors influencing stability and rate of degradation of a pesticide in water.

- Most of the available data on fate of pesticides in water are from laboratory studies; actual monitoring of forest streams to determine rate of dissipation has only been reported for some of the pesticides (e.g., hexazinone, trichlorfon, amitrole, and Bacillus thuringiensis.

- Except for carbaryl and fosamine ammonium which, at low concentrations, readily hydrolyze in water, chemical pesticides are generally stable to hydrolysis.

- Quantitative data on biodegradability in the aqueous environment have only been reported for a few pesticides; biodegradability appears to vary from that of readily biodegradable (e.g., dalapon and glyphosate) to considerable persistence (e.g., triclopyr, picloram, and simazine). Degradation pathways and products have been established for only certain of the pesticides (most notably hexazinone, carbaryl, and acephate).

- Photodegradation can be an important contributor to the dissipation of hexazinone, picloram, and triclopyr in the aqueous environment. Bacillus thuringiensis and nucleopolyhedrosis virus would be inactivated by prolonged exposure to sunlight. Although quantitative data have not been reported, the remaining pesticides are expected to be relatively stable to photodegradation.

3.2.5 Impact on Non-Target Plants and Organisms (Table 9)

- Many of the pesticides have been developed for specific applications (e.g., site preparation and/or release) and specific application conditions (application rates, time of application, application method, etc.) against specific target pests. Proper use is thus essential to achieve maximum efficacy and minimum damage to non-target species within the application area.

TABLE 8. SUMMARY OF DATA ON FATE IN WATER

Pesticide	Chemical Degradation	Microbial Degradation	Photodegradation	Miscellaneous
I. HERBICIDES				
Amitrole	Possible chemical degradation, but specific mechanism not reported.	Probable microbial degradation in water or sediments as in soil, but no specific data reported.	Amitrole reported to be stable under UV light.	Mechanism for degradation not reported. Disappearance from water may be due to dilution or adsorption to bottom sediments. No amitrole residue found in streams 3 days after application to 260 acres of forest land at 2 lb/acre.
Atrazine	No quantitative data available.	No quantitative data available.	Extremely slow, due to lack of sunlight adsorption. Expected to be insignificant in the environment.	Maximum of 16.7 ppb detected in 7 rivers monitored in corn belt; peak residue occured during month of heaviest application (May-June), and declined to < 1ppb for rest of year. Rate of decay in ponds treated with 0.3 ppm approximately 0.68 ppb/day (attributable to chemical and/or microbial degradation routes, uptake by aquatic organisms, adsorption to bottom soil, and/or other mechanisms).
Dalapon	Data unavailable; considered negligible based on rate of chemical degradation in soil.	Major route of degradation. BOD/COD ratios comparable to readily biodegradable susbtances such as sucrose and ethanol.	Quantitative data unavailable; considered insignificant in water based on behavior in soil.	—
Dicamba	Possible hydrolysis, but specific mechanism not reported.	Probable microbial degradation in water or sediments as in soil, but no specific data reported.	None reported.	Mechanisms for degradation not reported. May be hydrolyzed and slowly transformed to 5-OH dicamba (about 10% after 32 days).
2,4-D	Ester hydrolyzed to the acid. Half-life shorter at higher pH – ranges from 0.04 to 220 days depending on ester formulation and pH.	Favored in warm, nutrient-rich water. Esters hydrolyzed to the acid. In natural waters, may remain stable for 8 months or more.	Photodegradation not a major mechanism. Breakdown product is 2,4-dichlorophenol. Volatilization may be important for removal of some esters under low pH conditions.	Concentrations in forest streams following spraying are generally <100 ppb
Fosamine Ammonium	Aqueous solutions of 5 ppm concentration hydrolyzed nearly completely to CPA with 2 weeks at pH 5 (half-life, 10 days); no hydrolysis after 4 weeks at pH 7 and 9. At 7200 ppm (typical of actual spray concentrations) less than 3% decomposition observed at pH 5 and 7.	No data available.	Extremely slow under laboratory conditions (2% decomposition in 8 weeks of 5 ppm solution exposed to irradiation intensity of 1200 watts/sq cm). Expected to be insignificant in the environment.	—
Glyphosate	Does not degrade via chemical routes; no degradation observed of 0.1 ppm at pH 4 to 7.3 after incubation 49 days in the dark; or of 25 or 250 ppm at pH 3,6 and 9 following incubation at 5°C and 15°C in the dark for 32 days.	Major route of degradation in natural waters; half-life in water approximately 2 weeks.	Data unavailable; considered negligible based on rate of photodegradation in soil.	—

(Continued)

TABLE 8. (Continued)

Pesticide	Chemical Degradation	Microbial Degradation	Photodegradation	Miscellaneous
Hexazinone	Relatively stable to chemical hydrolysis under natural conditions (less than 1% degradation noted in test solutions over several weeks).	Microbial degradation (see Table 6) and photodegradation major causes of hexazinone reduction in natural waters.	In laboratory test solutions, 30% degraded in 5 weeks; rate slower in natural waters where sediments are present.	—
MSMA	Expected to be negligible.	Converted to a number of organic and inorganic arsenic compounds.	Does not photodegrade.	May also adsorb to sediments in water.
Picloram	Stable to hydrolysis under natural conditions.	Not readily decomposed by microorganisms in water.	Readily degraded by UV light and sunlight in water (photolysis half life of 5 to 60 days reported). Degradation thought to follow pseudo-first order kinetics. Numerous degradation routes possible, including free radical pathway.	—
Simazine	Considered moderately persistent in water; half-life 50 to 70 days, with 99% loss after 12 months. pH and temperature dependent; half life 4 months at 70°C, pH 7; shorter at increasing and decreasing pH.	Not considered a significant degradation route. Quantitative data unavailable.	Extremely slow under laboratory conditions; considered insignificant in the field. 4,6-bis (ethylamino)-s-triazine major degradation product.	—
Triclopyr	Minor; stable to hyrolysis in buffered solutions up to 9 months at pH 5, 7 and 8 and at 15, 25 and 35°C; less than 1% converted to 3, 5, 6-trichloro-pyridine.	Quantitative data unavailable; considered negligible relative to dissipation via photodegradation.	Major pathway for dissipation from aquatic environments. Decomposition rapid in both natural sunlight and under laboratory conditions; half life is 10 hrs at 25°C. Degrades to trichloropyridinol, which further degrades to various pyridine polyols via free radical mechanism.	—
II. INSECTICIDES				
Acephate	Expected to be minimal relative to microbial degradation.	Degrades faster in warmer water with higher pH; degradation faster when sediments present.	Does not photodegrade.	—
Carbaryl	Hydrolyzes rapidly in water at pH>7; no decomposition at pH 3-6. Half life one month at 3.5°C and 3.5 days at 20°C at pH 8.	Degrades to 1-naphthol, CO_2 and other products.	Subject to photodecomposition; rate dependent on pH, level of incident radiation and dissolved oxygen. During summer months in the field, rate as much as four times that in winter months.	Residue of 2 to 260 ppb found 2 to 3 hours after application of 1 lb/acre Sevin 4 oil to forest test plots.
Trichlorfon	Possible chemical degradation, but specific mechanism not reported.	Probable microbial degradation in water or sediments as in soil, but no specific data reported.	Half life shorter with exposure to sunlight.	Degradation faster under alkaline conditions and at warm temperatures. Half life <15 days under various pH, temperature conditions. Levels of 0.40 to 0.06 ppm detected in streams one hour after spraying and less than 0.002 ppm after 4 days following application of 1 lb/acre to forest plots.

(Continued)

TABLE 8. (Continued)

Pesticide	Chemical Degradation	Microbial Degradation	Photodegradation	Miscellaneous
III. BIOLOGICALS				
Bacillus thuringiensis	None reported.	None known.	Inactivatied by UV light.	No viable spores present in river water 4 weeks after aerial application to Canadian forest plots.
Nucleopolyhedrosis virus	None reported.	None known.	Inactivatied by UV light.	—
Pheromones	Possible chemical degradation, but specific mechanism not reported.	None reported.	None reported.	Mechanism for degradation not reported. Pink bollworm pheromone had half-life in water of 7 days.

TABLE 9. IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
I. HERBICIDES					
Amitrole	Phytotoxic to many agricultural plants	Low toxicity to fish (salmon 48 hr LC_{50} = 3250 ppm); toxic to Daphnia (48 hr LC_{50} = 3 ppm)	Field applications have produced depressed nitrification rate and decreased numbers of microorganisms	Relatively non-toxic to bees at recommended application rates. Less than 5 percent mortality to bees at a dose of 12.09 ug/bee, which is about eleven times the field dose (1.12 ug/bee) from application of 1 kg/ha. Low bird toxicity (oral LD_{50} > 2,000 mg/kg, mallard ducks). Low mammalian acute toxicity (oral LD_{50}, 1,100 mg/kg; rat, 14,700 mg/kg, mouse). Reported to be carcinogenic in mice and rats	Due to its high water solubility, amitrole is not expected 6 bioaccumulate
Atrazine	Extremely toxic to 5-week old red and white pine seedlings when applied at rates of 1,2 and 4 lb a.i./acre. Harmful to other nontarget species (grapes, soybeans, alfalfa, etc.) May persist at phytotoxic levels in soils for 1 – 2 years	Low to moderate toxicity to most species of fish (48-hr LC_{50}, 118mg/ℓ bluegills, 4.5 mg/ℓ, rainbow trout). 30% mortality to shrimp observed in 48-hr exposures to 1 ppm. Moderately toxic to lower aquatic organisms (e.g., mayflies, leeches, gastropods, etc).	Nontoxic to soil microorganisms. May be growth stimulant to certain populations of actinomycetes, bacteria and fungi	Low toxicity to birds and mammals (LC_{50} > 5000 for mallard ducks; 700 – 800 ppm for bobwhite quail; 3,850 mg/kg for rats.) Non-tumorigenic and embryotoxic (except at high levels – 800 to 2000 mg/kg in the rat)	Bioaccumulation low in aquatic biota (accumulation ratios 17, 8 and 9 for fish, snails and algae, respectively in aquarium concentration of 0.82 ppm). Some bioaccumulation in microorganisms. Maximum residues in fish were 5 ppm in rivers containing 16.7 ppb. Is metabolized readily by mammals; metabolites rapidly excreted with no bioaccumulation
Dalapon	Fairly selective for annual/perennial grasses and not harmful to conifers if applied several weeks before planting. Injury to conifers possible when used in combination with atrazine	Low toxicity to fish (LC_{50} > 100 ppm for many species). No effect level for snails and crustaceans is 200 ppm or greater	Considered non-toxic. Slight increases in populations of soil mites, millipeds and springtails observed after 20 lb/acre applied; no changes to earthworm population	Low acute toxicity to mammals (acute oral LD_{50} rat, 9300 mg/kg dalapon sodium salt; 5,660 mg/kg DOWPON and DOWPON M). Low subacute toxicity to to cattle, sheep. Low acute toxicity to birds (oral LD_{50} chickens, 5,600 mg/kg). No effects observed on reproduction of pheasants bobwhite quail and mallard ducks at 1,000 to 5,000 ppm	Little to no bioaccumulation in mammals, birds or aquatic organisms (feeding mammals and birds 100 – 1,000 ppm for several years gave tissue levels of < 100 ppm during treatments, and 1 ppm when feeding was discontinued)
Dicamba	Phytotoxic to many deciduous shrubs, trees, conifers and forbs	More toxic to fish than to birds or mammals (48-hr LC_{50} = 36 ppm for rainbow trout)	Data unavailable.	Low level of toxicity to birds and mammals (acute oral rat LD_{50} > 1,000 mg/kg; less toxic to birds). Relatively non-toxic to bees at recommended application rates. 2.6 percent mortality to bees at dose of 91 ug/bee, or about eighty times the field dose	Does not bioaccumulate. Studies in rats show excretion in urine

(Continued)

TABLE 9. (Continued)

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
2,4-D	Harmful to numerous crops; may damage conifers	Butyl esters 100 times more toxic than the acids; 96-hr LC_{50}'s about 1.0 mg/ℓ for trout. Effects on aquatic invertebrates at levels < 10 ppm	Quantitative toxicity data unavailable; 2,4-D readily decomposed by soil organisms (See Table 6)	Relatively non-toxic to bees at recommended application rates. 3.7 and 6.4 percent mortality to bees at doses of 24.17 ug/bee of 2,4-D sodium salt and 18.13 ug/bee 2,4-D low volatile oil-soluble ester (field dosage is 1.12 ug/bee). Few effects on birds observed. Peripheral neuropathy observed in persons exposed to 2,4-D at high doses; congenital malformations seen in rats or mice, few other effects observed. LD_{50}'s range from 300 to 5,000 mg/kg for poultry, mallard ducks, pheasants, pigeons and quail.	Based on several studies in fish and large mammals, 2,4-D does not bioaccumulate
Fosamine Ammonium	Phytotoxic to non-target woody plants, including conifer seedlings (at application rates of 2.25 or 4.5 kg/ha). Conifer tolerance higher during fall dormancy than spring/summer growth seasons	Low toxicity to fish and lower aquatic species (LC_{50} 670, > 1,000 and > 1,000 ppm for bluegills, rainbow trout and fathead minnow, respectively. 48-hr LC_{50} is 1,524 ppm for Daphnia magna. No data available on metabolism in fish	Considered nontoxic to soil organisims Populations of soil bacteria and fungi unaltered by 10 ppm for 8 weeks. May or may not affect rates of nitrogen fixation by soil bacteria	Low toxicity to mammals and birds (acute oral LD_{50} of 24,000 mg/kg for rats, 7,380 mg/kg for guinea pigs, > 10,000 mg/kg for mallard ducks and bobwhite quail.) No adverse effects except mild diarrhea noted from feeding rats 2,200 mg/kg/day for 14 days. Not teratogenic (10,000 ppm fed to pregnant rats) or mutagenic (Ames test)	Metabolized and/or excreted rapidly by animals and considered non-bioaccumulable. Typically > 85% eliminated in feces, and > 8% in urine. Low accumulation observed in catfish exposed to 1 ppm for 4 weeks
Glyphosate	Temporary browning of conifers observed in release applications using 1 to 2 qts/acre. No injury sustained by crops after agricultural application at usual rates. Injury to nontarget plants due to drift from forest application considered minimal	Low to moderate toxicity (96-hr LC_{50}, 2.3 mg/l for fathead minnows, 43 mg/l for mature scuds). Surfactant used in Roundup considered the principal toxic agent in the formulation (24-hr LC_{50} for rainbow trout, 140 mg/l for glyphosate, 2.1 mg/l for surfactant)	Has minimal-to-nil effect on organisims under aerobic and anaerobic conditions. No adverse effects observed from 5 and 25 ppm on microbial populations in soil in terms of nitrogen fixation; nitrification; and starch, protein or leaf litter degradation	Low toxicity to wildlife and beneficial insects (LC_{50} mallard duck and quail > 4,600 ppm; acute oral LD_{50} rat, 4,320 mg/kg; LD_{50} bee, 100 ug/bee)	Little to no bioaccumulation in fish (0.1 ppm Roundup in bluegills, trout and bass exposed to 10 – 12 ppm for 14 days; 80 ug/kg glyphosate in fish tissue and 60 ug/kg in fish eggs after exposure to 2.0 mg/l Roundup). Rapidly excreted in mammals (80% in feces, 11% in urine of rabbits 5 days after administration of single dose)

(Continued)

TABLE 9. (Continued)

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
Hexazinone	0 to 15% conifer mortality may occur in release applications, depending on conifer species, soil type and application rate. Residue levels in non-target wild fruits under study	"Slightly" toxic to fish and Daphnia (96-hr TL_{50} values of 275 to 420 ppm for three species of fish tested). Exposure to intermittent concentrations (6 to 44 ppb) of hexazinone in a forest stream did not result in major alterations in species composition or diversity in aquatic macroinvertebrate community	10 ppm hexazinone added to 3 agricultural soils did not reduce fungi or bacterial count in 8 wks; in lab bioassays, 100 ppm showed no fungal toxicity. 5 to 20 ppm hexazinone added to 2 soils had no effect on soil nitrifying bacteria in a 5 wk test. No major changes noted in the terrestrial microarthropod samples 8 months after treatment in a forest watershed study	Low toxicity to mammals and birds; acute oral LD_{50} of 860, 2,258 and > 3,400 mg/kg for guinea pig, mallard ducks and dog, respectively. Not carcinogenic, embryotoxic or teratogenic (5,000 ppm in diet of rat). No effect level in 2-yr rat feeding study was 200 ppm	Not bioaccumulative in fish. No evidence for accumulation in stream organisms in an 8-mo field study; but residue levels in terrestrial invertebrate were a maximum of two orders of magnitude greater than 0.01 to 0.18 ppm levels found in forest floor material
MSMA	Toxic to many agricultural and non-agricultural plants	Low toxicity (96-hr LC_{50}'s of 13 to 1,100 ppm for fish)	Relatively non-toxic	Toxic to some grazing animals. 48-hr LD_{50} for bees, 24 ug/bee	Bioaccumulation observed in some aquatic organisms but it is not expected to become concentrated in food chains
Picloram	Toxic to young conifers and various nontarget species; several incidents of damage reported due to spray drift. Certain crops injured as long as 5 years after application due to picloram persistence	Low toxicity to fish and other aquatic species (24-hr LC_{50} 230 ppm, rainbow trout; 64 ppm, fathead minnow). Increase in fry mortality in *Salmo clarki* observed at concentrations greater than 1.3 mg/ℓ. No adverse effects in food chain study with algae, *Daphnia*, goldfish and guppies. Inhibitory to growth of certain species of algae at 50 to 250 ppm. Picloram ester fromulations more toxic to fish than picloram and picloram salts due to presence of toxic impurity 2-(3, 4, 5, 6-tetrachloro-2-pyridyl) – guanidine	Very low toxicity to soil microorganisms; no adverse effects noted on treatment of 45 common soil organisms, including bacteria and fungi, with up to 1,000 ppm. Concentrations of 1 to 10 ppm inhibitory to populations of soil *Penicillia* but stimulated growth of *Aspergilla* and *Trichoderma*.	Low toxicity to birds. (Acute oral $LD_{50} > 2,000$ mg/kg for mallard ducks and pheasants). For bees, LD_{50} = 15 ug/bee for both picloram and a certain Tordon formulation. Low toxicity to mammalian species (oral LD_{50} 8,200 mg/kg, rats; > 1,000 mg/kg, sheep; > 750 mg/kg, cattle). No adverse effects in long-term feeding studies on rats. Tordon 101 considered more toxic than picloram to sheep (feeding 0.55 mg/kg resulted in 2 deaths within 10 days)	Excreted rapidly by and does not bioaccumulate in mammals (90 percent excreted in dog urine when fed at levels of 100 mg/kg in the diet). Not accumulated in invertebrates or in their food chains. Accumulation factors of 0.25 (picloram) for *Bambresia sp.* and 0.23 (picloram) and 0.050 (6-hydroxy-3.5-dichloro-4-aminopicolinic acid metabolite) for catfish

(Continued)

TABLE 9. (Continued)

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
Simazine	Causes severe injury when sprayed directly on young pine seedlings (based on reported rates of 0.5 and 1 lb a.i./acre). Phytotoxic to certain non-target agricultural and orchard species (e.g., oats, peach trees). Residues may persist at phytoxic levels into next growing season	Low toxicity to fish and lower aquatic organisms ($LC_{50} > 1,000$ ppm Princep 80W for bluegill and channel catfish). No effects on daphnid reproduction at 0.25 to 3.0 mg/ℓ	Harmless at normal application rates. Cellulolytic organism growth stimulated by normal and higher-than-normal application rates; nitrogen cycle organisms unaffected. Fungal populations in sandy loam soil stimulated by 2.5, 5.0 and 10.0 ppm in one reported study; minor fungicidal activity also reported in separate study	Low toxicity to mammals (acute oral $LD_{50} > 5,000$ – 10,000 mg/kg for rats, mice, rabbits). No systemic toxicity observed in 2-yr rat feeding study with 100 ppm. Very low toxicity to birds (no mortality up to 5,000 ppm to bobwhita quail and mallard ducks). No effect on mallard duck reproduction at dietary levels of 2.0 and 20.0 ppm. No insecticidal activity at normal application rates	Low in fish and other aquatic organisms. No accumulation observed in fish, dragonfly nymphs, midge larvae and mayflies in four 0.25-acre ponds treated with 0.1, 0.3 1.0 and 3.0 µg/mℓ. Accumulation of one to four times the water concentration observed in other studies. Metabolized rapidly by animals and not accumulated in tissue or milk (80 ppm in cow diet resulted in 0.01 to 0.02 ppm in milk). Little bioaccumulation by micro-organisms; equilibrium tissue concentration reached after 24 hours in static studies
Triclopyr	Minor injury to conifers at 4.4 kg/hr reported in release application; no injury at 2.2 kg/hr. Some inhibiition of cucumber yields at 0.5 lb a.i./acre after 3 months; 50% inhibition at 3 and 9 lb a.i./acre after 4 months	Low toxicity; 96-hr LC_{50} for bluegills, 148 ppm (triclopyr) and 891 ppm (Garlon 3A); for rainbow trout, 117 ppm (triclopyr), 552 ppm (Garlon 3A); shrimp, 895 ppm (Garlon 3A)	Considered non-toxic; no effect observed on 6 soil microorganisms at 500 ppm after 72 hrs incubation	Low toxicity to mammals and birds; acute oral LD_{50} rat, 630 mg/kg (triclopyr), 2,140 mg/kg (Garlon 3A), 2,140 mg/kg (Garlon 4); LC_{50}, mallard duck, > 5000 ppm (triclopyr), > 10,000 ppm (Garlon 3A), > 10,000 ppm (Garlon 4). Non-carcinogenic to mice and rats. Mildly fetotoxic at 200 mg/kg/day. Data unavailable on insects	No bioaccumulation in fish; data unavailable for mammals, birds, etc.

(Continued)

TABLE 9. (Continued)

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
II. INSECTICIDES					
Acephate	Not expected to harm plants; slight leaf burn and interveinal chlorosis has been reported	Low toxicity to fish (96-hr $TL_{50} > 1{,}000$ ppm)	None reported	May inhibit brain cholinesterase activity in birds but mortality not expected at recommended application rates. Toxic to non-target insects; toxic to bees (LD_{50} 1.2 ug/bee). Low toxicity to mammals (acute oral LD_{50} 700 mg/kg, rat. Low to moderate toxicity to birds (acute oral LD_{50} 350 mg/kg, ducks; 825 mg/kg chickens).	Slight bioaccumulation has been observed in fish; acephate is reported to be eliminated as concentration in water drops
Carbaryl	Low phytotoxicity. Some injury may occur to certain species (e.g., apples, pears, boston ivy) if rain/high humidity persist for several days after application	Toxic to fish (96-hr LC_{50} 1 – 20 ppm). Degradation product 1-naphthol also toxic. Toxicity varies with formulation (e.g., 48-hr LC_{50} 28 ppm for Sevin-4-oil, 14 ppm for Sevin 40 WP). Toxic to crustaceans and mollusks (96-hr LC_{50} 10 ppb – 3 ppm) and certain other aquatic organisms. 10 ppm lethal to three species of marine algae; 0.1 ppm lethal to five species to phytoplankton.	Toxic to soil microbes; decrease in microarthropod population in millet field litter observed 3 weeks after treatment with 2 lbs/acre. Degradation product 1-naphthol also toxic (lethal at 50 ppm to *Fusarium solani*; 20 – 30 ppm to certain bacteria). Toxic to certain soil microbes	Moderate to low toxicity to mammals (LD_{50}'s typically 200 – 850 mg/kg). Low toxicity to birds (LD_{50}'s 780 – 2,030 mg/kg). No significant effects on reproduction. Toxic to honeybees (LD_{50} 1.3 µg a.i./bee), and certain soil and aquatic insects	Bioaccumulates in aquatic biota (accumulation ratio 1,064 in trout bile; and 3.6 and 4.0 for lake trout and Coho Salmon in aquarium concentrations of 2.6 ppm). Little bioaccumulation in mammals (accumulation ratio 0.01 for cow kidney, 0.006 for chicken kidney)
Trichlorfon	No adverse effects reported	Highly toxic to some aquatic invertebrates (e.g. *D. magna*, 48 hr $LC_{50} < 1$ ppb); less toxic to fish (LC_{50} generally from 1 to 100 ppm)	No effects observed when applied at levels up to 10 ppm	Adverse effects on many insects observed; low toxicity to bees (LD_{50} 59.83 ug/bee). Reduced brain acetylcholinesterase levels found in birds but no mortality observed. Low to moderate toxicity in mammals (acute oral LD_{50} to rats, 184 mg/kg as technical formulation; 2500 mg/kg, as 1.5 oil); depressed cholinesterase levels reported; teratogenic in rats; used in veterinary practice to kill pests on animals	Analysis of fish tissues indicated no bioaccumulation. Did not bioaccumulate in sheep.

(Continued)

TABLE 9. (Continued)

Pesticide	Plants	Fish and Other Aquatic Organisms	Soil Organisms	Birds, Beneficial Insects and Mammals	Bioaccumulation Potential
III. BIOLOGICALS					
Bacillus thuringiensis	Quantitative data unavailable; no adverse effects expected	Generally low toxicity; some toxicity to Coho salmon juvenile at > 300 – 1,800 billion/kg viable spore count	Quantitative data unavailable; no adverse effects expected	Non-toxic to bees at levels as high as 726,000 spores/bee. Non-toxic to rats up to 24g/kg body weight. May be harmful to some non-target Lepidoptera	Quantitative data unavailable; no bioaccumulation expected
Nucleopolyhedrosis virus	Quantitative data unavailable; no adverse effects expected	Non-toxic to fish. Laboratory studies with Coho salmon, Chinook salmon and steelhead trout showed no adverse effects from exposure via 3 routes: waterborne exposure, intraperitoneal injection and feeding	Quantitative data unavailable; no adverse effects expected	Low toxicity to birds, mammals, bees. No adverse effects at concentration of 10×10^9 polyhedra/bee hive. Non-carcinogenic to rats	No bioaccumulation in fish. None expected in other species
Pheromones	Quantitative data unavailable; no adverse effects expected	No quantitative data available; no adverse effects expected	Quantitative data unavailable; no adverse effects expected	Several pheromones found non-toxic in laboratory animals. Flying insects, birds, etc. could get caught in sticky traps	Quantitative data unavailable; no bioaccumulation expected

- Many of the pesticides are phytotoxic to agricultural crops and other non-target plants, and hence can potentially cause damage to such crops and plants if drifted significant distances off-target; in forestry applications, however, potential for spray drift can be minimized via strict adherence to label instructions and local buffer zone requirements. Herbicide formulations which can be used as large pellets (e.g., "Velpar" "Gridball" formulation of hexazinone) or in special devices such as luretape, rubber caps, or wicks (e.g., in the case of pheromones) present little potential for drift during the application.

- Certain laboratory bioassay data for aquatic organisms have been reported for nearly all the pesticides addressed. These data indicate: (a) a range of toxicities with LC_{50} values being in the 1 to 100 ppm range for amitrole, dicamba, 2,4-D (butyl ester), glyphosate, picloram (ester formulations), carbaryl and trichlorfon; (b) for some pesticides (e.g., 2,4-D, carbaryl, and picloram) toxicity is different for different formulations; (c) toxicity effect is dependent on the species tested and is generally higher for the organisms in the lower end of aquatic food chains (e.g., reported 48-hr LC_{50} values for Daphnia are 3 ppm and less than 1 ppb for amitrole and trichlorfon, compared to values for fish of 3,250 ppm and 1-100 ppm, respectively).

- Quantitative data on impacts on organisms in the forest soils under actual application conditions and the long term significance of such impacts are generally unavailable for many of the pesticides. Short term toxicity data reported for dalapon, fosamine ammonium, glyphosate, hexazinone, picloram, simazine, triclopyr, carbaryl, and trichlorfon indicate variable impacts (non-toxic to growth stimulants), depending on the species and the application rate.

- Based on data from animal studies, the majority of the pesticides addressed would be considered to be of low acute toxicity to mammals and birds; LD_{50} values for rats are generally greater than 1,000 mg/kg and tests with atrazine, hexazinone, fosamine ammonium, glyphosate, picloram, triclopyr indicate LD_{50} values for mallard duck ranging from 700-800 mg/kg for atrazine to greater than 10,000 mg/kg for fosamine ammonium. Quantitative toxicity data for bees indicate low to high toxicity to bees, with LD_{50}'s of 100, 24, 15, 1.3, and 1.2 µg/bee for glyphosate, MSMA, picloram, carbaryl, and acephate, respectively. Bacillus thuringiensis has been shown to be non-toxic to bees at levels as high as 726,000 spores/bee.

- Bioaccumulation data indicate low or no potential for bioaccumulation in fish for nearly all pesticides for which such data have been reported, except for carbaryl for which a high bioaccumulation factor in fish and certain fish organs has been observed. Little or no bioaccumulation in test birds and mammals has also been noted for atrazine, dalapon, dicamba, 2,4-D, fosamine ammonium, glyphosate, picloram, simazine, carbaryl, and trichlorfon. Biological insecticides are not expected to accumulate in fish or other organisms.

APPENDIX

I. HERBICIDES

II. INSECTICIDES

III. BIOLOGICALS

I. HERBICIDES

Common Name:	Amitrole
Chemical Name:	3-amino-1,2,4-triazole
Major Trade Names:	Amitrol-T; Cytrol Amitrole-T; Weedazol
Major Applications in Forestry:	Control of salmonberry and elderberry in the coast range of Pacific Northwest.

SUMMARY

Amitrole is a non-selective herbicide that is absorbed through leaves or by roots. In plant tissue, it inhibits chloroplast development, causing chlorosis and eventual death. It is currently registered for use as a herbicide on non-agricultural sites, and is used primarily to control grasses, broadleaf weeds, poison ivy and aquatic weeds. In forestry, it is used for site preparation and for conifer release.

Amitrole is highly soluble in water but is not soluble in non-polar organic solvents such as oils. It is not tightly bound to soils and, thus, can be leached readily. In addition, it is microbially or chemically degraded in soil. The persistence of amitrole in soil is considered low to moderate and depends on the soil type and soil conditions. Reported half-lives range from several days to six weeks. In plants and in the soil, amitrole is converted to compounds with little or no known toxicity. Amitrole does not accumulate in animal tissues nor is it biomagnified in food chains.

Amitrole is relatively toxic to a number of agricultural crops. It is also highly toxic to the aquatic invertebrate Daphnia with a 48-hour LC_{50} of 3 ppm. Amitrole is relatively non-toxic to coho salmon with a 48-hour LC_{50} of 3250 ppm. It has low toxicity to birds and to honey bees. The acute oral toxicity of amitrole to rats and mice is moderate to low with LD_{50}'s of 1,100 and 14,700 mg/kg, respectively. However, amitrole has been reported to be carcinogenic in both rats and mice, and it has been reported to be mutagenic. Consequently, use of amitrole on food crops has been suspended.

1.0 INTRODUCTION

Amitrole is a non-selective, systemic herbicide registered under the Federal Insecticide, Fungicide and Rodenticide Act in 1956 (1). One of the early uses of amitrole was on cranberry bogs after harvest. In 1959, certain lots of cranberries containing amitrole residues were removed from the market following reports that amitrole induced cancers of the thyroid in rats (1,2). By 1971, all registered uses of amitrole on food crops were cancelled (2). Amitrole is currently registered with the Environmental Protection Agency for non-crop and aquatic site use (1).

Amitrole's primary use is for control of grasses and broadleaf weeds, poison ivy, poison oak and aquatic weeds (3). In the forestry industry, amitrole is applied to salmonberry and elderberry for site preparation and conifer release in the coast range of the Pacific Northwest (4,5). It is generally applied as a foliar spray at the rate of about 2 pounds of active ingredient per acre.

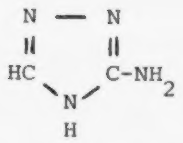
Amitrole is marketed in the United States by Union Carbide, Custom Chemicals, American Cyanamid, and Fairmont Chemicals under several trade names, including the following (1,3):

- Amerol
- Amino Triazole Weedkiller 90
- Amitrol-T
- Amizol
- Azole
- Cytrol
- Cytrol Amitrole-T
- Herbizole
- Weedazol.

It is also available commercially as a mixture of herbicides with simazine, diuron, atrazine, bromocil, fenac and linuron (3,6). Formulations are available as soluble powder and liquid and in pressurized containers. Some amitrole formulations contain ammonium thiocyanate, NH_4SCN. The NH_4SCH reportedly enhances translocation of the herbicide inside the target plant by inhibiting the formation of a less mobile metabolite (2,7).

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF THE ACTIVE INGREDIENT

The active ingredient of amitrole formulations is 3-amino-1,2,4-triazole:



It is a weak base which reacts as a typical aromatic amine (2). The ring structure of amitrole is resistant to hydrolysis and the action of oxidizing agents (8).

Amitrole is highly soluble in water (28 grams in 100 grams water at 25°C) and in the polar organic solvent ethanol (26 grams in 100 grams at 75°C). It is insoluble in oil or in most other non-polar organic solvents. Amitrole is reported to have a low volatility although no vapor pressure values are reported in the literature. Its melting point is 159°C (6).

3.0 ENVIRONMENTAL FATE

Since very little environmental fate data has been published in connection with the use of amitrole in forests, most of the discussion in this section is based on data for non-forest applications.

3.1 UPTAKE AND METABOLISM BY PLANTS

Amitrole is absorbed through the leaves and roots of plants and readily translocated inside the plant (2). Its mode of action is to prevent chloroplast development in new growth, possibly by interfering with purine synthesis (9) or by preventing normal carotenoid synthesis and accumulation (10).

Upon review of the literature, Carter (2) states there is no conclusive evidence of extensive ring cleavage in plants. The amitrole residues found in treated plants are in the form of free amitrole or conjugates reversibly bound to plant constituents. Bondarenko (11), in a field study of treated soybeans and corn, found amitrole throughout the plants eight days after application. In a laboratory study, amitrole was detected in grafted, treated tomato plants for up to 3-1/2 months after treatment (12).

More than a dozen compounds derived from amitrole have been isolated from treated plants (13). Most of these compounds are probably conjugates (2). One metabolic breakdown product has been identified as 3- (3-amino-s-triazole-1-yl) 2-aminopropionic acid or 3ATAL (14). The metabolite, 3ATAL, appears to be less toxic than amitrole and, therefore, amitrole is considered to be detoxified when metabolized to 3ATAL. The 3ATAL is also not as mobile in plants as amitrole. The additive NH_4SCN inhibits 3ATAL formation (15,16) and, thus, may indirectly enhance amitrole mobility (16).

Amitrole in the plant exhibits its phytotoxicity in the form of a chlorosis or lack of chlorophyl in new growth which is white in color. Phytotoxicity is related to the amount of amitrole in the soil, ambient temperature and soil pH (12,17,18). Muzik (12) has observed higher phototoxicity to grafted tomato leaves at an ambient temperature of 55°F compared to temperatures of 70°F and 85°F. Phytotoxicity to cucumber plants has been shown to be maximum at a soil pH of 6.5 (17).

3.2 FATE IN SOIL

In the soil amitrole may be found adsorbed to soil colloids or in the form of complexes with metallic ions (nickel, cobalt, copper, iron, and magnesium) (18). Disappearance from soil may be the result of uptake by plants, volatilization, photodecomposition, leaching, microbial degradation or chemical breakdown. Volatilization is not considered a major factor in the loss of amitrole from soil because of the low volatility of amitrole (19,20,21). Photodecomposition is probably also not important because amitrole appears to be stable under ultraviolet radiation (21,22). However, in laboratory experiments, photodecomposition has been shown to occur under uv light in the presence of riboflavin (2,21).

Persistence of amitrole in soil is dependent to a large extent on adsorption of the compound on soil colloids and on its chemical/microbial degradation. These factors, which affect the potential for leaching and hence, for contamination of surface waters, are discussed below.

3.2.1 Adsorption and Leaching

In studies of amitrole fate in soil, adsorption is usually measured as the change in amitrole concentration before and after addition to soil (23, 24). Day, et al. (20) found that 20-50 percent of the amitrole applied to 55 California soils was reversibly adsorbed to the soil accompanied by a decrease in amitrole mobility. Repeated percolation of water through the soil released the bound amitrole. No relationship was found between adsorption of amitrole and base exchange capacity or soil classification. However, Martson, et al. (25) report that amitrole adsorbs rapidly and tightly to soils with high base exchange capacity and organic matter content. Other researchers have also found the adsorptive capacity of soil to be related to organic matter content. Kaufman, et al. (26) found that adsorption of amitrole in organic soil was as high as 40 percent and in inorganic sandy soil as low as 3 percent. Nearpass (23) measured amitrole adsorption in a high organic soil suspension of peat and water. Over 59 percent of the amitrole applied was adsorbed onto the soil after one minute; over 68 percent was adsorbed in 24 hours. Adsorption also increased with increasing acidity in the soil.

In a given soil type, the adsorptive capacity for amitrole appears to directly affect its leaching characteristics. Leaching of amitrole can occur in sand or sandy loam but is greatly reduced in clay, clay loam or high organic soil (27). These latter soil types show stronger affinity for adsorption of amitrole. Day, et al. (20) studied adsorption and leaching in several soil types. As expected because of amitrole's high solubility in water, amitrole moves readily with the leaching water. Repeated passage of water released more amitrole. Peak concentrations of amitrole recovered in the first few passages of water were found in those soils exhibiting poor adsorption. High adsorptive soils required more water to release the bound amitrole.

3.2.2 Persistence and Degradation

Amitrole is considered to have a low to moderate persistence in soil, depending on the soil type and conditions. Detectable residues are reported to persist from several days to six months or more (28,29). In a study measuring amitrole residues by methanol extraction from forest litter, amitrole was shown to degrade fairly rapidly with a half-life of about 5 days (28). Kaufman (29) found residues amounting to 36 percent of the applied amitrole after 18 months in a sandy loam soil. Burschel and Freed (30) report a breakdown rate of 1.31 µg/g soil/day at 29°C for a Chehalis loam soil and estimate a half-life of about 6 weeks.

Factors influencing persistence of amitrole in soil include soil moisture, temperature, pH, base exchange capacity and soil treatments aimed at eliminating or inhibiting soil microorganisms (see Table 1). Ercegovich

TABLE 1. EFFECT OF SOIL PARAMETERS ON PERSISTENCE OF AMITROLE IN SOIL

Soil Parameter	Range of Parameter Tested	Increasing the Parameter Produces (+) increase, (-) decrease, (0) no effect*			
		Adsorption	CO_2 Evolution	Phytotoxicity	Recoverable Residues
Moisture, %	0 - 30%				- (21)
Temperature, °C	15 - 100°C			- (12)	- (21)
pH	4.3 - 8.0	- (23)		- (31)	- (21)
Base exchange capacity, meq/100 gms	3 - 99	+ (2,20)			+ (18)
Clay content, %	2 - 15%			- (20)	- (18)
Organic matter content, %	1.5 - 75%	+ (26)			- (18)
Treatment with KN_3			- (26)		
Treatment with ethylene oxide			- (26)		
Autoclave treatment			- (26)		
Addition of free-radical reagents			+ (22)		
Presence of dalapon in soil				0 (29)	

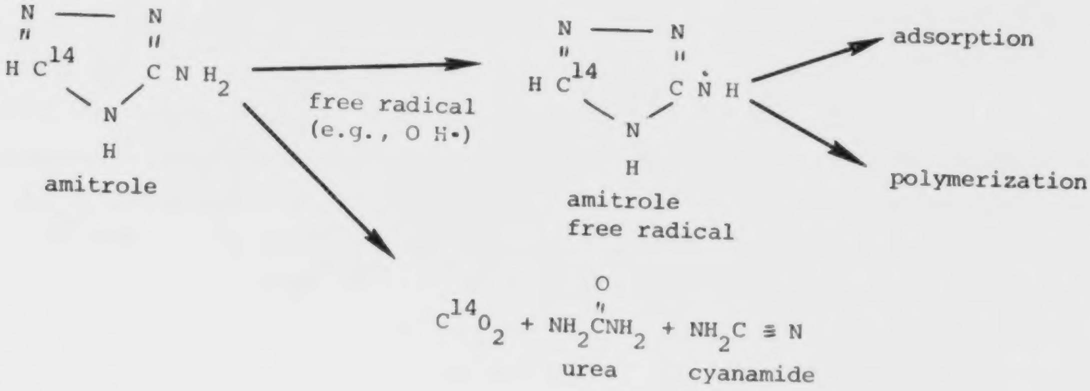
*Numbers on the designations refer to the reference for the data source.

and Frear (21) studied the effects of various soil parameters on the persistence of amitrole. They found that increased soil moisture decreases persistence probably by enhancing degradation or leaching. Elevated temperatures to 100°C also shortened residue life. The fact that amitrole steadily disappeared under increasingly high temperatures to an extreme of 100°C indicates that degradation is at least partially a chemical process rather than strictly microbial decomposition. Deviation of pH much above or below neutral also shortened persistence (21). This observation is consistent with phytotoxicity studies showing that amitrole has optimum efficiency in soil with a pH of about 6.5 (17,31). Sund (18) studied the effect of soil type on amitrole degradation and persistence and discovered that a high base exchange capacity (about 100 meq per 100 grams of soil) increased persistence whereas high clay and organic matter content decreased persistence. This finding is in agreement with Day, et al. (20) who found that high colloidal soils were characterized by decreased persistence of amitrole.

Degradation in soil has been measured as: (a) evolution of radioactive CO_2 from soil containing ^{14}C-5 amitrole (22,26); (b) loss of phytotoxic effect, measured in terms of reduced plant growth (29); and (c) reduction in the amount of recoverable amitrole (18,19,21). Evolution of $^{14}CO_2$ from ^{14}C-5 amitrole containing soil has been taken as evidence of ring cleavage. Because CO_2 or formate is formed from the 5 carbon of amitrole and labelled amitrole is commercially available only as ^{14}C-5 amitrole, other degradation products remain unlabelled and would be difficult to identify and quantify (2).

Several investigators have found that autoclave treatment of soil nearly stops CO_2 evolution from amitrole-containing soils (20,21,26). Autoclaving also depresses the amitrole degradation rate as measured by amitrole soil residue depletion over time (20,32). Kaufman, et al. (26) also found that sterilization by ethylene oxide or treatment with inhibitory chemicals that stop microbial activity do not stop CO_2 evolution but do reduce it substantially. These findings suggest that degradation of amitrole in soil is not entirely a microbiological process but that some degradation involves chemical reactions (see below). The possible chemical nature of degradation is further supported by observed CO_2 evolution from amitrole in the presence of free radicals (22,26).

Plimmer, et al. (22) propose the following scheme to show the possible pathway of the degradation and adsorption of amitrole.



The free radical extracts a hydrogen, converting amitrole to a free radical that can either adsorb to colloidal particles or polymerize. The amitrole can also be oxidized by the free radical to form CO_2, urea and cyanamide as primary products that would be readily utilized by soil microorganisms. CO_2, urea and cyanamide have been identified as breakdown products in free radical systems (22).

There has been much debate over whether microorganisms or chemical reactions are primarily responsible for degradation (2). Evidence for chemical decomposition of amitrole stems from success in generating $^{14}CO_2$ from free radical systems and the seemingly contradictory results obtained from soil sterilization studies. As noted previously, sterilization by ethylene oxide does not completely stop CO_2 evolution as does autoclaving. However, ethylene oxide is not as damaging to free radical systems or extracellular enzymes as is autoclaving. Involvement of such enzymes in amitrole degradation could explain the effects of different methods of soil sterilization.

Efforts to isolate soil organisms that degrade amitrole have been, for the most part, unsuccessful. Compacci, et al. (33) have isolated several soil bacteria of the genera Pseudomonas, Bacillus, and Corynebacterium that will degrade amitrole after a 3-week lag period and sufficient dilution. Evidence that microorganisms can degrade amitrole in a laboratory setting is not sufficient proof that microbial degradation occurs to any appreciable extent in nature. Kaufman, et al. (26) propose that microbes per se are not responsible for amitrole degradation but are indirectly involved in enhancing or providing the conditions that allow for chemical decomposition.

3.3 PERSISTENCE IN WATER

Amitrole persistence in water has not been studied extensively. Norris, et al. (34) monitored amitrole residues in forest streams before and after aerial application of 2 lbs per acre to 260 acres of forest land. Amitrole residues appeared within an hour of application, peaked in about 2 hours and could not be detected by the third day. Norris (35) also studied the effects of rainfall on amitrole concentration in streams flowing by or through treated forest areas. The area was treated in late March and samples of creek water were taken in late September and early October with average rainfall of 0.63 inches per day. No measurable amitrole residues were detected. Demint, et al. (36) have determined that amitrole residues in treated irrigation canals are less than 1 ppb and hence, insufficient to damage sensitive crops. (The canal banks had been treated with amitrole for weed control at about 4 lbs. per acre.)

A long-term study of amitrole degradation in water and sewage treatment systems was carried out by Ludazck and Mandia (37). Using 94 percent pure amitrole, they were unable to detect significant BOD, COD, or any measurable degradation of amitrole in distilled water, sewage or river water. In respiration tests there was a stimulation of CO_2 production from biodegradable material in river water but no decrease in the concentration of amitrole. An inhibitory effect on respiration and nitrification in activated sludge was observed in the presence of amitrole concentrations between 2.2 and 10 ppm. Disappearance of amitrole in water may be due mainly to dilution and perhaps to a much lesser extent to adsorption to bottom sediment.

4.0 IMPACTS ON NON-TARGET ORGANISMS

4.1 PLANTS

Amitrole is phytotoxic to many agricultural plants including tomato plants, cucumber seedlings, citrus and avocado trees, and wheat (20,29,31, 38).

4.2 ANIMALS

The toxicity of amitrole to animal species has been reviewed by Maier-Bode (39) and Pimental (40). In mallard ducks, the oral LD_{50} was greater than 2,000 mg/kg (41). The LC_{50} for mallards, for pheasants and for Japanese quail was greater than 5,000 ppm when these birds were given an amitrole-containing diet for 5 days (42). The 48-hour LC_{50} for salmon was estimated to be 3,250 ppm (43). Bluegill, green sunfish, lake chub-sucker and small-mouth bass fry have tolerated 50 ppm for 8 days (44).

Daphnia is very sensitive to amitrole with a 48-hour LC_{50} of 3 ppm (4). The median immobilization concentration for amitrole to Daphnia magna is reported to be 23 ppm (45). The EPA recommended safety measures, based on Daphnia sensitivity, limit amitrole potable water concentrations to 0.15 to 0.015 ppm and irrigation water concentrations to 0.1 to 0.01 ppm, depending on stream size (48).

When bees were dusted with amitrole at a dose of 12.09 μg/bee, mortality was less than 5 percent (46). For comparison with field conditions, an application rate of 1 kg/ha would give a dose of 1.12 μg/bee. Therefore, at recommended application rates, amitrole is considered relatively non-toxic to bees.

The National Institute of Occupational Safety and Health data on mammalian toxicity is presented in Table 2. Amitrole has moderate to low acute oral toxicity to mice and rats. However, it has been reported to be carcinogenic in both mice and rats. In addition, mutation studies using a host-mediated assay test system in which mice were exposed to the test chemical and Salmonella typhimurium was used as the indicator organism, indicate 12 mg/kg as the lowest dose reported to have a mutagenic effect (47).

4.3 MICROORGANISMS

Amitrole's effect on microorganisms has been studied by several investigators. Valentine and Bingham (49) cultured three genera of freshwater algae, one of which metabolized the amitrole, producing three cellular and four extracellular breakdown products. Field applications of amitrole at recommended rates of 8, 4, 2, and 1 lb per acre have produced a depressed rate of nitrification and decreased numbers of microorganisms (38). In

TABLE 2. TOXICITY OF AMITROLE TO MAMMALS (47)

Organism	Toxicity	Comments
Rat	Oral LD_{50}: 1,100 mg/kg	
Rat	Oral TDL_0: 122 g/kg	Toxic effects reported: carcinogenicity.
Mouse	Oral LD_{50}: 14,700 mg/kg	
Mouse	Oral TDL_0: 113 g/kg	Toxic effects reported: carcinogenicity.
Mouse	Ipr LD_{50}: 200 mg/kg	
Rat	Oral TD: 3,670 mg/kg	Toxic effects reported: neoplastic effects.

other studies, amitrole has been found to inhibit microbial respiration and nitrification in activated sludge (37), nitrifying bacteria in soil (50) and cellulose decomposition in fungi at concentrations of 500 ppm in buried soil samples (51).

4.4 BIOACCUMULATION

No major concern has been reported regarding bioaccumulation of amitrole, probably because of amitrole's high solubility in water and insolubility in cellular lipids (6,48). Bioaccumulation of amitrole has not been studied to any appreciable extent.

5.0 MISCELLANEOUS

The EPA Advisory Committee on amitrole has expressed concern over the labelling of ammonium thiocyanate as an inert ingredient in commercial amitrole formulations (1). Ammonium thiocyanate has an acute oral LD_{50} for rats that is very much lower than that for amitrole (760 mg/kg vs. 2500-1100 mg/kg) (6). Ammonium thiocyanate is a reactive compound, a goiterogen and inhibits the metabolic breakdown at amitrole (1).

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Common Name: Atrazine

Chemical Name: 2-chloro-4-ethylamino-6-isopropylamino-s-triazine

Major Trade Names: AAtrex (80W, 90W, 4L, 4CL)

Major Applications in Forestry: Used primarily in the Pacific Northwest in conifer release, nursery applications and seed orchards and production areas for grass and broadleaf weed control.

SUMMARY

Most of the available information on the fate of atrazine in soil and water is the result of laboratory and/or field studies with agricultural systems. Very little data are available on or in connection with applications to forests.

Atrazine is considered a stable, persistent herbicide and may persist in phytotoxic concentrations for over a year in agricultural soils. High concentrations of soil organic matter, such as may be present in forest soils, as well as low temperatures, tend to increase its persistence. Atrazine degrades via chemical and microbial routes; the extent of and factors affecting such degradation in forest soils have not been fully investigated. The extent of atrazine losses due to volatilization from agricultural soils is very small. Such losses are expected to be even less from forest soils due to lower temperatures. Atrazine decomposes by uv light; the extent of photodecomposition in forest systems is expected to be very low.

Atrazine is considered a low mobility herbicide. Leaching and desorption of atrazine are lowest in soils with high organic matter content, and hence should be low in forest soils. Atrazine is slightly soluble in water. It has been measured in rivers near application sites following heavy rainfalls. Atrazine degrades to some extent in water.

Atrazine is phytotoxic tc numerous non-target plant species. It is extremely toxic to very young, recently-emerged red and white pine seedlings. Atrazine is only slightly toxic to fish, moderately toxic to lower aquatic organisms, and reportedly has no insecticidal activity. It is relatively nontoxic to mammals. Bioaccumulation is low in fish, moderate in microorganisms, and nil in animals.

Inert ingredients present in atrazine formulations are not considered hazardous.

1.0 INTRODUCTION

Atrazine is a selective herbicide that has been widely used in crop and non-crop applications for broadleaf weed and grass control since its discovery, as one of a family of s-triazine herbicides, in the early 1950's (1). It currently leads all other herbicides in the U.S. in volume of use (2).

In the forest industry, atrazine is used in conifer release, nursery applications of fir transplants, and seed orchards and seed production areas on Douglas-fir, Noble fir, western hemlock, lodgepole pine and Ponderosa pine (3,4). These uses are primarily in the Pacific Northwest west of the crest of the Cascade Range. Usual application rates for atrazine are 3-5 lb of 80 percent active ingredient (in 10-20 gallons of water) per acre for conifer release; 2 lb a.i./acre in nursery applications; and 2-4 lb a.i./acre (3) in seed orchards and production. AAtrex 80W is one of the principal wettable powder formulations used in all three applications (3). Application methods for conifer release are typically the aerial broadcast method or ground spot applications (3,4). Atrazine is sometimes used in combination with 2,4-D or Dalapon (3-5 lb a.i./acre) for more effective control of broadleaf weeds as well as grass for Douglas-fir release in Pacific Northwest forests (5). Atrazine has also been used to a limited extent in forests in the southern U.S. in combination with simazine.

Agricultural uses of atrazine are extensive and include application to corn, sorghum, sugarcane, pineapple and other crops (6). It is also used in vegetation control in rangeland (6). After uptake by plant roots, atrazine exerts its toxic action on plants by inhibiting photosynthesis with arrestation of the Hill reaction in chloroplasts; atrazine also interferes with plant transpiration (7,8). Atrazine is manufactured domestically by Ciba-Geigy Corp. under the trade name AAtrex, Shell, Farmland and Vicksburg Chemical Companies (9). It is also manufactured by foreign producers under the trade name Atranex (Israel) and Vectral SC (Great Britain) (10).

Atrazine formulations are 50-80 percent wettable powders in 5-lb multiwalled bags and a 4-lb/gallon flowable concentrate available in 1- and 5-gallon containers (2). The wettable powder formulations contain one or more inert materials including: (a) carriers, such as calcium silicates, sodium aluminum silicates, or precipitated silicic acid; (b) wetting agents, such as arylalkyl sulfonates; and (c) dispersing agents, such as lignin sulfonates. Chalk or clay may also be added to some formulations (1).

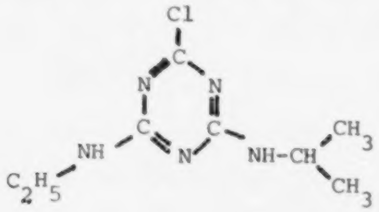
Atrazine is also formulated in combination with several other herbicides, as (6):

- AAtram 20G (atrazine plus propachlor)
- Atratol 8P (atrazine plus sodium chlorate and sodium metaborate)
- Atratol 80W (atrazine plus prometon)
- Bicep 4.5L (atrazine plus metolachlor)

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The chemical nomenclature for atrazine is:

2-chloro-4-ethylamino-6-isopropylamino-s-triazine



It is a white crystalline solid with a melting point of 173-175°C.

Solubility in water is 70 ppm (7,11,12); in methanol, 18,000 ppm (11); in ether, 12,000 ppm (11); and in chloroform, 52,000 ppm (11).

Vapor pressure data are shown below as a function of temperature (6):

Temperature, °C	mm Hg
10	5.7×10^{-8}
20	3.0×10^{-7}
30	1.4×10^{-6}
50	2.3×10^{-5}

3.0 ENVIRONMENTAL FATE

Based on the literature reviewed in this program, it appears that the fate of atrazine in the forest environment has not been adequately addressed. Most of the fate information reported and discussed below pertains to non-forest environments.

3.1 UPTAKE AND METABOLISM IN PLANTS

Extensive studies have been conducted on the uptake of atrazine from corn, sorghum, cereals, weeds and other plants. These studies, which have been reviewed by Kearney (1), have focused on uptake of atrazine from nutrient solutions in laboratory experiments and in many cases actual field conditions have not been adequately simulated. The studies indicate that the principal mechanism of uptake is through the plant roots, although uptake through leaves also occurs; root uptake occurred readily in all species studied. Research using radiolabelled atrazine showed that it is evenly distributed through the system into all aerial parts of the plants, with some accumulation in the marginal zones of the leaves, particularly in susceptible species. Root uptake increases with increasing concentration of atrazine, time of exposure, higher temperature and lower relative humidity. Foliar uptake occurs much less readily than root uptake, and is enhanced by addition of adjuvants such as mineral oil (1). Atrazine exerts its toxic action on plants by inhibiting photosynthesis, resulting in defoliation and plant death.

Metabolic degradation of atrazine in plants occurs via 4 major mechanisms: (1) hydrolysis of the 2-chloro group to give hydroxy atrazine; (2) conjugation with glutathione or amino acids at the 2-position of the triazine ring; (3) N-dealkylation of side chain groups; and (4) s-triazine ring cleavage (1,13,14). The degradation route and rate vary with plant types, with stage of growth and with site of entry of atrazine into the plant.

In corn the major metabolite is the 2-hydroxyl hydrolysis product, formed both in the roots and shoots (1,15). Cleavage of the triazine ring occurs to only a minor extent in corn (as well as in cotton and soybeans) after 4 days as indicated in a recent study by Davis, et al. (16). However, the ring cleavage is a difficult and relatively slow process and occurs after longer periods of time (1). In range grasses, 175 to 270 days after treatment with 16 lb a.i./acre, residues included hydroxyatrazine (<0.04 ppm) and N-dealkylation products such as deethylated atrazine (0.72-1.15 ppm), deisopropylated atrazine (0.17-0.25 ppm), and 2-chloro-4,6-diamino-s-triazine (0.5 ppm) (14). Residues in range grasses were not determined beyond 270 days.

In general, hydrolysis and conjugation with glutathione and amino acids occur readily in monocotyledonous plants (i.e., sorghum, cordgrass) (14,17).

N-dealkylation (deethylation or de-isopropylation) can either precede or follow formation of hydroxyatrazine in these species (14). Hydrolysis and conjugation of atrazine result in a complete loss of phytotoxic properties. Plant species which hydrolyze and/or conjugate atrazine are most resistant to the herbicide. N-dealkylation of atrazine results in only partial loss of phytotoxicity, and species using this route of degradation have moderate resistance to atrazine (1).

3.2 FATE IN SOIL

The fate of atrazine in soil can be described in terms of six factors: volatilization, photodecomposition, leaching, adsorption, runoff, and chemical and microbial degradation. These factors are discussed below.

3.2.1 Volatilization

The extent of atrazine volatilization from soil is not fully known. Atrazine is known to dissipate from treated areas by volatilization but it is generally held that this does not take place to a significant extent (2, 6), presumably due to the low vapor pressure of atrazine. Although quantitative results are unavailable, atrazine losses by volatilization have been measured and were observed to occur in the field most prevalently 1-2 days after initial application, and occurred to the greatest extent under conditions of high temperature and direct prolonged sunlight prior to rainfall (6,18).

Laboratory studies of atrazine on planchets at 25°C and 60°C by Foy (19) showed significant losses of atrazine even at the lower temperature. Kearney (1,20) extended this study to measuring triazine losses from five soils as a function of soil type. Although insufficient data were obtained to permit definite conclusions on the relationship between rate of volatilization and soil properties, atrazine was observed to volatilize from all of the soils. Vapor losses of atrazine from a variety of other surfaces, including sand, clay, metal and glass, have also been observed and measured in the lab by Davis (16).

In addition to temperature, volatilization is also affected by soil moisture, with increased volatilization from drier soils (21,20). In the forest, the extent of atrazine volatilization from soil due to sunlight exposure may be less than in the field due to increased shading. Also, because atrazine is somewhat amphoteric in nature, the pH of aqueous solutions may be expected to influence its volatility; the extent of this influence has not been determined (11).

3.2.2 Photodecomposition

On the soil surface (and on the surface of vegetation) atrazine undergoes photodecomposition due to the action of uv radiation in sunlight (22). The rate of photodecomposition and factors influencing it are not fully understood (6). Available data indicate that photodecomposition occurs to some extent in the field if high temperatures and prolonged sunlight follow application before precipitation (6), but these conditions are not considered typical of the forest environment. Studies conducted by Comes and Timmons (23) on agricultural fields indicate losses of 47 percent and 60 percent during exposure to spring sunlight for 25 and 60 days, respectively. Under forest conditions the rates of atrazine decomposition on the soil surface would be less than in the agricultural fields due to increased shading.

The mechanism and products of photodegradation in soil have not been investigated. The decomposition of atrazine on other surfaces has been studied in the laboratory. Atrazine exposure to UV light on aluminum planchets at 42°C resulted in a change in the UV absorbance and a color change from white to light tan (24); the degradation products were not identified. One possible product is hydroxy atrazine, which is a known photodecomposition product of atrazine under exposure to light of 253.7 nm in aqueous solution (25).

3.2.3 Adsorption and Leaching

Atrazine is generally considered a low solubility, low mobility herbicide (12,26,27). In the soil atrazine is readily and reversibly adsorbed on soil particles (2,7). The extent of adsorption (and desorption) is a function of soil type as well as temperature, moisture, and pH (26,28). Soil organic matter is the primary soil parameter responsible for adsorption, with increasing organic matter resulting in increased adsorption (29). In other studies it has been shown that atrazine is also more readily adsorbed on clay soils than on soils with low clay content (6).

Adsorption of atrazine increases with the lowering of the pH, particularly in clay soils, since atrazine is somewhat basic, and at higher pH levels it loses its affinity for negatively charged clay particles (14). High levels of soil moisture facilitate hydrolysis of atrazine adsorbed to clay soils, and indirectly decrease the amount available for desorption (14). The extent of adsorption is also higher at lower temperatures.

Adsorption capacity of a given soil type for atrazine affects the potential for leaching of atrazine from soil. The leaching tendency would be lower with those soil types and under those conditions which promote adsorption. In general, leaching is more pronounced in sandy and clay soils than in soils with high organic matter content (30). In agricultural soils with high organic matter content, atrazine is not normally found below the upper foot of soil in detectable quantities, even after years of continuous use (26,27). In a study by Burnside (31), leaching of atrazine in Nebraska soils was determined to be greater in coarse-textured, low organic matter soil in western Nebraska even though the rainfall in this region was considerably less than in regions with high organic content soils (32). Even in sand the depths to which atrazine penetrates via leaching are not significant. When atrazine was surface-applied to Plainfield sand at rates of 1, 2, and 4 lb/acre and leached, most remained in the first inch of soil when 2, 4, and 8 inches of water were used (27). Some atrazine moved downward to a depth of 6 inches; with application of additional water more atrazine was leached from the first inch of soil. Even after prolonged leaching, atrazine is not expected to penetrate the soil to any significant depth. Smith, et al. (33) observed that atrazine applied to irrigation ditches at a rate of 22.4 kg/ha did not leach to depths greater than 90 cm after 3 years. Marriage, et al. (34) found that residues of atrazine applied at a rate of 4.5 kg/ha for 9 consecutive years to the same plots of a peach orchard located on a sandy loam soil near Harrow, Ontario, were confined to the upper 15 cm of the soil profile and that the majority of the herbicide remained in the 0-5 cm soil layer. The maximum residue level found was 0.4 kg/ha of atrazine in the top 15 cm of the soil profile.

Even though leaching of atrazine from the forest soil has not been studied, based on the data presented above, the extent of such leaching would be expected to be lower than that in agricultural soil because of the higher organic content of the forest soil.

3.2.4 Runoff

Although atrazine is slightly soluble in water, a potential exists for buildup in high concentrations in local waterways due to runoff after heavy rainfall (2). This is particularly true if rainfall occurs soon (1-2 weeks) after application.

In a field study, Leonard, et al. (35) determined the amount of atrazine in runoff (water plus sediments) from sandy loam soils at a Piedmont watershed in Georgia as a function of application rate (1.45 to 4.03 kg/ha) and time after application (up to 60 days). During the experiment an average rainfall of 30 cm was observed. The results indicated a nearly exponential decrease in atrazine concentration with time. The total quantity of atrazine measured in the runoff ranged from 0.2 to 0.8 percent of the original atrazine applied. In a field study by Triplett (36) on 0.4- to 3.5-ha watersheds, the highest concentrations of atrazine (0.48 ppm) were present in runoff occurring soon after application and declined rapidly in later events. The quantity of atrazine transported increased with the amount of rainfall and was inversely related to the length of time between the application and the runoff event. A maximum of 6 percent of the applied herbicide was transported from the field even under the most favorable conditions, and the average for all watersheds was less than 2 percent.

A summary of other atrazine runoff studies is presented in Table 1. The results indicate that atrazine runoff is a function of the amount, frequency, and intensity of runoff events.

Based on atrazine runoff data and data on runoff with other pesticides, Leonard, et al. (35) developed the following empirical relationship (for the Georgia Piedmont soil tested) which correlates the concentration of herbicide in runoff (y, mg/l) with the concentration of residual herbicide in the soil at the time of runoff (x, mg/g): $y = 0.05\ x^{1/2}$. This empirical relationship has not been tested against other soil types or other concentration ranges.

3.2.5 Chemical and Microbial Degradation

Atrazine is considered to be a stable, persistent compound. The persistence of atrazine in soil was reviewed by Sheets (41) who concluded it is very persistent, and that residues can persist in agricultural soils at phytotoxic levels for over one year. More recent studies by Best, et al. (42),

TABLE 1. SUMMARY OF SELECTED ATRAZINE RUNOFF STUDIES

Location/Soil Type	Application Rate	Time Span	Rainfall	Results and Comments	Reference
Fallow plots of Cecil soil (6.5% slope)	3 lbs/acre	96 hrs after herbicide application	10 year frequency storm (2.5 in/hr)	Atrazine loss of 7.3% observed.	37
Field plots of Hagerstown silty clay loam growing corn	0, 0.6, 1.1, 2,2, 4.5, 6.7, and 9.0 kg/ha	One growing season (1967)	Rainfall experienced at Pennsylvania test site in 1967	Average losses for all rates in 1967 in runoff water and soil sediment equalled 2.4% and 0.16% of the total applied, respectively.	38
Field plots of Hagerstown silty clay loam growing corn and alfalfa	2.2 and 4.5 kg/ha	1971 and 1972 growing seasons	Rainfall experienced at Pennsylvania test site in 1971 and 1972	Total losses of atrazine during first growing season were 5.0 and 4.8% of application rate; 87 to 93% of the losses occurred within the first month following application.	39
16.4 ha corn field	1.7 kg/ha	1976 growing season	Rainfall experienced at site in 1976	First storm event occurred 11 days after application and discharged 55% of the total runoff loss of the 1976 growing season and 90% of the total runoff loss occurring within 2 months of planting.	40

Ritter, et al. (43), and Buchanon and Hiltbald (44) have indicated that atrazine rarely persists at phytotoxic levels longer than 1-2 years. The residual activity of atrazine in soil for many specific soil types is such that most rotational crops can be planted one year after application, except in an arid or semi-arid climate. However, broadcast rates needed in heavier, relatively higher organic matter soils of the North Central states result in enough residue carryover, under some conditions, to injure small grains, alfalfa and soybeans planted 12 months later (6,45).

The persistence of atrazine in a soil has been the subject of a large number of studies, the results of some of which are summarized in Table 2. These studies show that the persistence is greater in soils with lower organic content, at greater depths and at lower temperatures.

The atrazine degradation in soil occurs via chemical and/or microbial routes. In a study of atrazine persistence, Hunter, et al. (50) found atrazine residue at phytotoxic levels in desert soil eight years after application. The desert soil was characterized by high pH, low moisture, and extreme surface temperatures - conditions which do not favor chemical and microbial degradation of atrazine. A brief review of the factors affecting chemical and microbial degradation of atrazine in soil follows.

Chemical Degradation

Hydrolysis is the major chemical degradation reaction of atrazine in soil. The reaction is first order and involves hydroxylation of the carbon-chlorine bond to give hydroxy atrazine (51,52). The activation energy of the hydrolysis reaction is 10.8 kcal/mole, which corresponds to the energy required to break the C-Cl bond (22). The rate of hydrolysis is pH dependent and the reaction is both acid and base catalyzed. The following half-lives have been measured for atrazine hydrolysis as a function of pH (53):

pH	Half-life (days)
1.3	5.1
2.2	18.4
3.1	66.4
11.1	81.1
11.9	15.2
12.9	12.9

TABLE 2. SUMMARY OF SELECTED ATRAZINE PERSISTENCE STUDIES

Location/Soil Type	Application Rate	Soil Depths Measured	Time Span	Results and Comment	Reference
17 sites in the U.S., including central Washington, Alabama, Maryland and Minnesota	N.A.	3,9 and 15 inches	Samples placed at beginning of growing season; retrieved in fall	Between <1 and 58% of the original atrazine was recovered; atrazine persisted longer at lower depths and was more persistent in the northern U.S. (average recoveries showed 61% more at 15-in. level than at 3-in. level)	46,1
Boddington barn field soil (1.6%C, 16% clay, 11% silt, 73% sand, pH 7.4), and Triangle Field soil (4%C, 16% clay, 16% silt, 68% sand, pH 5.4), 80% water holding capacity	5 mg/g	N.A.	Soils were incubated at 22°C for 3-4 weeks	First order degradation rate was used to describe the results; in Boddington barn soil the rate was faster at high pH levels but the reverse occurred on Triangle soils, probably due to increased chemical hydrolysis on the higher organic content triangle soil	47
Sandy loam soils in:					
Colorado	2 lb ai/acre	0-6 in.	283 days	0.09 ppm	14
		6-12 in.	283 days	0.05 ppm	
	4 lb ai/acre	6-12 in.	283 days	0.5 ppm	
Montana	1,2,4 lb ai/acre	0-6 in.	130;320 days	All showed 0.05 ppm	
		6-12 in.	130;320 days		
Nevada	1.2 lb ai/acre	0-6 in.	365 days	0.07 ppm	
		6-12 in.	365 days	0.05 ppm	
	2.4 lb ai/acre	0-6 in.	365 days	0.25 ppm	
		6-12 in.	365 days	0.15 ppm	
Idaho	1.2 and 2.4 lb ai/acre	0-6 in.	365 days	0.005 ppm for all	
		6-12.	365 days		
	9.6 lb ai/acre	0-6 in.	365 days	0.10 ppm	
		6-12 in.	365 days	0.05 ppm	
Sharpsburg silty clay loam	0.5-2 ppm	15,40 and 90 cm	0-41 mos.	Phytotoxic acids of atrazine dissipated during the first 5 mos. at 15 cm, and during the first 17 mos. at 40 cm. Atrazine residues remained at 90 cm depth after 41 mos.	32
Loam soil	2-20 lb ai/acre	0-1 in. 1-2 in. 2-4 in. 4-6 in. 6-8 in.	One growing season	After rainfall of 8.16 in., 85.3% of atrazine was in the 0-1 in. layer; 5.7% in the 1-2 in. layer. After one year the results were the same.	48
Irrigation ditch soil in Tyron, Nebraska; Valentine loamy fine soil	2.5 lb/acre	6-18 in.	73 days	No atrazine detected	18
	10 lb/acre	6-12 in.	319-366 days	No atrazine detected	
	30 lb/acre	1-18 in.	0.05 ppm	Persisted one year after application	
	30 lb/acre	18-36 in.	73 days	No appreciable atrazine detected	
Alabama	--	--	--	Half-life was measured at 30 days.	49

Based on the half-lives data, the average values of the rate constants for acid and alkaline hydrolysis have been calculated as 3.4×10^{-5} M^{-1} sec^{-9} and 6.5×10^{-5} M^{-1} sec^{-1}, respectively (53).

Studies on sterilized soil systems indicate that hydrolysis may be catalyzed by certain soil compounds. Nucleophilic compounds in soil including Fe/Al ions promote nucleophilic displacement of -Cl with -OH at high pH, whereas humic acid and various soil colloidal particles catalyze hydrolysis at low pH. The low pH hydrolysis results from the protonation of ring or chain nitrogen atoms and subsequent cleavage of the C-Cl bond (54). In general, increasing organic matter in soil increases degradation by chemical hydrolysis (1).

Several studies have been conducted on the formation and stability of nitrosoatrazines in soils. Results indicate that nitrosoatrazine is not formed in amounts that are significant at normal rates of field application of atrazine (2 ppm in the surface 7.5 cm of soil or 2 lb/acre application rate), and in the presence of 100 ppm NH_4NO_3 (14,55). In the presence of 100 ppm $NaNO_2$ (as N), nitrosoatrazine formed and increased in concentration with decreasing pH (% of atrazine converted to nitrosoatrazine as a function of pH were: pH5, 0%; pH4, 0.7%; pH3, 19.3%; pH2, 35.7%) (14,55).

Microbial Degradation

Microbial degradation accounts for the decomposition of a significant portion of atrazine in soil (6). Factors influencing microbial growth include soil moisture, temperature, pH, soil type and presence of nutrients, but very few studies have been performed measuring the effect of these factors on microbial degradation of atrazine. Three major routes for biological degradation are dealkylation, ring cleavage and hydroxylation of the 2-chloro group. Dealkylation is the primary mechanism of microbial degradation. Kaufman and Blake (56) observed atrazine degradation by dealkylation by 12 different fungi in a basal salts medium supplemented with sucrose; some of the fungi (i.e., Rhizopus stolonifer) removed the isopropyl group to give 2-chloro-4-ethylamino-6-amino-s-triazine) while others (i.e., Aspergillus fumigatus) removed the ethyl group to give 2-chloro-4-amino-6-isopropylamino-s-triazine. In a two-week study using chain-labelled atrazine, Skipper, et al. (57) found ethylamino ^{14}C in carbon dioxide involved by Aspergillus fumigatus.

Atrazine degradation by ring cleavage was studied by Roeth, et al. (58) and McCormick and Hiltbold (59) who observed the evolution of $^{14}CO_2$ from microbial cultures containing ^{14}C ring-labelled atrazine. The atrazine hydrolysis product hydroxy atrazine was also observed to undergo ring cleavage. Skipper, et al. (57) found that mixed microbial populations degraded the hydroxy atrazine ring three times more rapidly than it degraded atrazine. Ring metabolism of hydroxy atrazine was also found in a study with both aerobic and anaerobic lake sediment samples by Hance and Chesters (60) using ring-labelled hydroxy atrazine. More labelled carbon dioxide was evolved from aerobic than anaerobic sediment samples; however, the reverse was true for soil samples. Microbial degradation of atrazine by hydrolysis to hydroxy atrazine is known to occur by one microbial species, Fusarium roseum (22).

Both dealkylated and hydroxylated atrazine degradation products are subject to further microbial degradation (1). Recent studies have shown that degradation of both types of products may give rise to common metabolites, such as 2-hydroxy-4-amino-6-alkylamino-s-triazine (1,61).

3.3 PERSISTENCE IN WATER

Very limited studies have been conducted on the persistence and degradation of atrazine in water. Klaasen (62) studied the distribution and decay of atrazine applied to pond water in various components of a pond ecosystem. The study was carried out in farm ponds near Manhattan, Kansas to which atrazine was added to establish an initial concentration in water of 0.3 ppm. Atrazine levels were monitored in various pond ecosystem components (water, mud, fish, etc.). Soon after application residues were found at high levels (165-353 ppb) in all components except tadpoles. Residues decreased slightly during the growing season, but were still present at fairly high levels at the end of the growing season. The results of one set of experiments carried out in 1973 are shown in Table 3. As indicated in the tables, a rate of decay of 0.676 ± 0.367 ppb/day was calculated for the water.

In an atrazine water monitoring program conducted in 1975 in seven major rivers in the central U.S. (i.e., the corn belt), a maximum of 16.7 ppb of atrazine was detected. The peak residues occurred during the months of heaviest application (i.e., May-June); residue concentrations declined after June to ≤ 1 ppb for the rest of the year (14).

TABLE 3. ATRAZINE RESIDUES (PPB) AND RATE OF DECAY IN PONDS TREATED WITH 0.3 PPM ATRAZINE (62)

Sample Type	Days after Treatment					Slope and std. dev.	R^2
	0	1	22	55	120		
Surface water	ND[†]	309	230	237	206	.676 + .367	.63
Mud from shallow area	ND	323	314	302	284	.323 + .022	.99
Mud from deep area	ND	316	305	221	204	1.001 + .322	.83
Zooplankton	ND	240	277	213	195	.535 + .304	.61
Clam	--[‡]	--	--	250	--		
Bullfrog tadpole	ND	ND	--	--	--		
Small bluegill	ND	280	289	307	216	.568 + .358	.56
Medium bluegill	ND	270	237	290	230	.333 + .359	.17
Large bluegill	ND	290	245	260	211	.555 + .214	.77

*Pre-treatment

[†] ND = Not detectable (less than 0.4 ppb)

[‡] --= Samples could not be obtained

The rate of atrazine photodecomposition in water is extremely slow, as measured under laboratory conditions, and is not expected to be significant in the environment. This is primarily due to its lack of absorption of sunlight. Laboratory photolysis of atrazine in water and other hydrolytic solvents (e.g., methanol) at 253.7 nm was shown to result in the formation of the 2-hydroxy compound, due to nucleophilic displacement of the chlorine atom (53). In a related study, Jordan, et al. (24) observed that the uv spectrum of an atrazine solution was altered after irradiation with 253.7 nm light or with sunlight (292 to 400 nm).

4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

4.1 PLANTS

Atrazine has been shown to be phytotoxic to non-target forest species under certain application conditions. In one study by Kozlowski (27), atrazine applied in nursery culture as a soil spray at rates of 1, 2, and 4 lb a.i./acre was extremely toxic to young, recently-emerged (5-week old) red and white pine seedlings. No harmful effects were reported on older seedlings. Atrazine combined with dalapon (3-5 lb a.i./acre) and used for conifer release from grass in southwestern Oregon resulted in complete defoliation of well-established Ponderosa pines 8 to 15 feet tall (5). The severity of the damage was believed due to a synergistic effect of atrazine with dalapon.

Atrazine also exhibits phytotoxicity to a number of nontarget agricultural crops including soybeans, alfalfa, and small grains. It may persist at phytotoxic levels in agricultural soils for 1-2 years and may cause injury to susceptible species planted in the growing season following application (6). However, applications of 3.2, 6.4, 12.8, and 25.6 lb/acre of atrazine repeated annually to plots of Emperor variety grapes in Davis, California, gave no evidence of adverse effects (63).

Several studies have been conducted on the phytotoxicity to nontarget organisms of atrazine degradation products. The results indicate that hydroxy atrazine is non-phytotoxic. The ability of a plant to hydrolyze atrazine is a partial basis for its resistance to the herbicide. N-dealkylation products are moderately phytotoxic. This was confirmed in a recent study by Kaufman and Blake using oat seedlings (56). Hydroxy atrazine was shown to be non-phytotoxic to oat seedlings at 1 and 5 ppm concentrations. The N-dealkylation products 2-chloro-4-amino-6-isopropylamino-s-triazine and 2-chloro-4-ethylamino-6-amino-s-triazine were phytotoxic to oat seedlings; the former compound at both 1 and 5 ppm, and the latter compound at 5 ppm.

Recent investigations have shown that the protein content of various crops may increase when sublethal concentrations of triazine herbicides are applied. In a study by Singh, et al. (64), foliar application of 0.5 or 1.0 mg/l atrazine (applied until runoff occurred) increased the protein content in pods of bush beans and leaves of spinach under field and/or growth room conditions. Results of quantitative analyses indicated that the soluble amino acid content was also higher in the treated test species. In addition, the Fe content in the bush bean seeds and the Fe, Mg, P and K contents in spinach leaves were higher in the treated plants than in the controls (64). In studies conducted on MSMA and cacodylic acid, it has been shown that the presence of atrazine facilitates uptake of arsenic in green plants (1).

4.2 FISH AND OTHER AQUATIC ORGANISMS

Atrazine is slightly toxic to most species of fish and moderately toxic to lower aquatic organisms (2). Toxicological investigations conducted on goldfish and bluegill sunfish have shown atrazine to have very low toxicity toward these species (48-hour LC_{50} of 118 mg/l for bluegills) (6,12). However, atrazine is considerably more toxic to rainbow trout (LC_{50}=4.5 mg/l). Data on the toxicity of atrazine to various lower aquatic organisms were obtained in a study by Butler (65) in 1965, the results of which are shown in Table 4. As indicated in the table, shrimp are more sensitive to atrazine than fish or oysters and experience 30% mortality at 1.0 ppm atrazine in 48-hour exposures.

In acute and chronic aquatic toxicity studies by Walker (66), atrazine applied to fish ponds at rates of 0.2 to 6.0 ppmw was shown to be somewhat toxic to bottom fauna. Among the most sensitive organisms were mayflies (*Ephemeroptera*), caddis flies (*Tricoptera*), leeches (Hirudinea), and gastropods (Musculium). The most significant reduction in bottom fauna occurred during the period immediately following application. The bottom fauna appeared to recover four to six months after treatment. Walker (67,68) also found that an application of 0.5-2.0 ppm of atrazine to pond enclosures reduced clams to 1/8 of their original numbers, whereas the snail population increased by nearly 4 times. Portmann, et al. (69) found LC_{50}'s for the shore crab (*Cascinus maenus*) and the cockle (*Cardium edule*) to be greater than 100 ppm, while the brown shrimp LC_{50} was 10-30 ppm.

Vivier and Nisbet (70) experimented with atrazine in A361(I) and in Gasaprime (II) and found that for I, 0.5 ppm was lethal in 72 hours for 20% of the population of the minnow *Phoxinus phoxinus* while the 48-hour TL_m was 1.25 ppm. The 24-hour and 48-hour TL_m values for II were 3.75 and 2.5 ppm, respectively. Jones (71) found at least 90% survival for 72 hour exposures, for the fry of *Micropterus salmoides* (5.0 ppm) *letalurus punctatus* (10.0 ppm) and *Lepomis macrochirus* (10.0 ppm). No effect levels at concentrations of 10 ppm were found for *Erimyzon sucetta* (eggs), *Lepomus macrochirus* (eggs), and *L. cyanellus* after eight to ten day exposures (72). Small-mouth bass died after 3 days exposure at 10 ppm.

TABLE 4. TOXICITY OF ATRAZINE TO ESTUARINE ORGANISMS (65)

Oysters	Shrimp	Fish[§]	Phytoplankton
96-hr EC_{50}[*] ppm (mg/l)	48-hr EC_{50}[†] ppm (mg/l)	48-hr LC_{50}[‡] ppm (mg/l)	Percent decrease at 1.0 ppm
no effect at 1.0	30% at 1.0	no effect at 1.0	---

[*] Concentration of herbicide in sea water causing a 50% decrease in oyster shell growth.

[†] Concentration of herbicide in sea water causing mortality or paralysis to 50% of adult shrimp tested.

[‡] Concentration of herbicide in sea water causing 50% mortality to juvenile fish.

[§] Spotfish, Leisetomus Xanthurus.

In field experiments in Kansas, six experimental 1/10 acre ponds were exposed to 0, 20, and 150 μg/l of atrazine for 135 days (14). The ponds contained natural aquatic communities and controlled stocks of fish. Atrazine application resulted in an almost immediate decline in rates of photosynthesis by aquatic algae. The decline in photosynthesis rate was followed by increased growth of resistant plant species within a few weeks, resulting in significant alterations in the plant community during the course of the study (14). Other results of the study are summarized in Table 5. As indicated in the table, atrazine also reduced the photosynthesis of algae at 20 μg/l concentration level (14).

Very little data are available on the degradation products of atrazine in fish or in lower aquatic organisms. In one study on the metabolism of atrazine in box crabs, various water-soluble metabolites from glutathione conjugation of atrazine were observed (17).

4.3 WILDLIFE

Atrazine has low toxicity to warm-blooded animals. The acute oral LD_{50} for rats is 3,800 mg/kg and for mice, 1,750 mg/kg (6). Little data are available in the literature on toxicities of atrazine to birds and wildlife

TABLE 5. EFFECTS OF ATRAZINE (20 AND 500 µg/liter) ON POND ECOSYSTEM (14)

A. Water Quality and Algae

- Physical-chemical conditions: not directly affected.
- Oxygen and pH: indirectly lowered for 28 days due to effects on algal photosynthesis.
- Algal photosynthesis: within 2 days - in 500 µg ponds, declined by 96% --- in 20 µg ponds, declined by 34%.
- Algal photosynthesis: in 500 µg ponds, averaged 50% lower than controls --- in 20 µg ponds, similar to controls.
- Algal biomass: within 7 days in 500 µg ponds, declined by 50% --- in 20 µg ponds, similar to controls.
- Algal biomass: in 500 µg ponds, averaged similar to controls after 15 days.
- Algal composition: affected throughout the 135 days at both atrazine levels.
- Resistant algal species: increasingly dominant in ponds at both atrazine levels; first noticeable after 15 days.
- Resistant algal communities: in 500 µg ponds by day 56, 7X more resistant (photosynthesis) than control pond communities to another 500 µg.
- Resistant algal communities: in 20 µg ponds by day 85, no increased photosynthesis resistance but 2X more resistant to light energy blockage.
- Persistence of atrazine in the ponds: 75% of the original concentrations on day 116.
- Persistence of effects of this remaining atrazine demonstrated by exposing control pond algae to atrazine pond water on day 98.

B. Other Aquatic Organisms

- Aquatic flowering plant (Najas): reduced in biomass by day 15 by 100% with 500 µg and by 40% with 20 µg.
- Zooplankton reproduction rates (Simocephalus, Daphnia): reduced by 57% and 70% with 500 µg and 9% and 70% with 20 µg.
- Zooplankton biomass: reduced by day 15 by both atrazine levels up to 60% with 500 µg.
- Zooplankton composition: affected throughout 135 days by both atrazine levels.
- Zooplankton responses: indirect from the effects of atrazine of algae, their food source.
- Bottom-dwelling invertebrates (Fingernail clam, isopod, damselfly): no mortality response.
- Fish growth (gizzard shad, channel catfish, bluegill sunfish): reduced by 20%-30% with 500 µg and unaffected with 200 µg.
- Fish mortality: unaffected by atrazine.
- Fish offspring: from bluegill sunfish, reduced by 96% at both atrazine levels.

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species (i.e., deer, beaver, rabbits, etc.). However, a toxicological investigation conducted on bobwhite quail, pheasants, and mallard ducks showed atrazine to have very low toxicity to these species; the LD_{50} values for mallard ducks were >5,000 ppm; for pheasants, were >5,000 ppm; and for bobwhite quail, were 700 to 800 ppm of atrazine fed for five days, followed by three days of untreated feed (6,73). Studies conducted on cattle, dogs, horses fed a diet of 25 ppm atrazine or more over extended periods of time resulted in no observable ill effects (6).

In subacute toxicity studies (74), administration of daily dosages of 100 ppm of an 80% wettable powder formulation of atrazine to cows for 21 days, or feeding 30 ppm of this formulation in grain to cattle for four weeks resulted in no observable effects. In acute oral toxicity studies by Palmer and Radeleff (75), the toxic dosage of atrazine for cattle was found to be 25 mg/kg after 8 doses by drench and 2 doses by capsule. The toxic dosage for sheep was 5 mg/kg, although one sheep received 199 consecutive doses at 50 mg/kg before it was poisoned and died. Chickens administered 10 doses at 50 mg/kg had significant reductions in weight gains (75).

Innes, et al. (76) found no significant indication of tumorigenicity in rats fed 21.5 mg/kg atrazine at 7-28 days of age and then 82 ppm after 28 days of age. Rats fed 100 and 1000 ppm for two years showed no differences from controls (77). The administration of atrazine at a level of 46.4 mg/kg to C3H, C57, and AKR mice produced no significant increase in anomalies in offspring (78). Peters and Cook (79) determined that atrazine was not embryotoxic except when administered at extremely high levels (800 and 2000 mg/kg) to the rat. In addition, atrazine did not affect the number of pups per litter or weaning weight at levels as high as 1,000 ppm. Innes, et al. (80) found that oral administration of 83 ppm of atrazine to certain strains of mice did not cause a significant increase in tumors.

4.4 BENEFICIAL INSECTS

Limited studies on atrazine have shown no insecticidal activity (6). The synergistic effects of atrazine with insecticides on bees were studied by the U.S. Department of Agriculture (81). Bees were fed insecticides and insecticides fortified with atrazine or other herbicides at dosages which were determined sublethal in preliminary experiments. In no case was the mortality significantly greater feeding the bees herbicide-insecticide combination than feeding the insecticide alone at the same concentrations.

4.5 MICROFLORA

Atrazine is nontoxic to soil microorganisms (2). A number of studies conducted in recent years have shown varying results as to the impact of atrazine on soil microbial populations (82). Atrazine was shown to be a growth stimulant to microflora in a recent study by Percich (82). Increases in populations of actinomycetes, bacteria and fungi were observed in Conover loam soil treated with atrazine at rates of 10, 30, and 100 mg/g; the increases were also sustained for 2-3 months. The results confirmed investigations performed in the Soviet Union (83,84,85). Increases in populations of Fusarium, which led to increased root diseases in plants, have also been observed in atrazine-treated soils (82).

Comparative studies performed by Voets, et al. (86) showed that atrazine applied at a rate of 4 kg/ha in an orchard of dwarf apple trees reduced the populations of anaerobic bacteria, sporeformers, cellulolytic microorganisms and nitrifying, amylolytic and denitrifying microbial groups. A metabolic study has indicated no adverse effects on earthworms.

4.6 BIOACCUMULATION

The bioaccumulation of atrazine in fish, snails, and algae is "low" (see Table 6); in microorganisms, "moderate"; and in animals, "nil". (7,55). In a study of atrazine residues in 7 major rivers and tributaries in the Midwest in 1975, the maximum residues in fish were estimated at 0.5 ppm for a maximum residue concentration in the waters of 16.7 ppb. For a near-normal 1.0 ppb level in water, the concentration in fish was estimated at 0.02 ppm (14).

Bioaccumulation of atrazine in microorganisms was demonstrated in a recent laboratory study of 18 species of actinomycetes and fungi in water, nutrient broth and loam soil containing 5 ng/ml (mg/g for soil) of atrazine (82). Among the species studied, there was a large variation in the ability to accumulate atrazine. Less accumulation occurred in soil than in water, due to restricted contact of the organisms with the atrazine in soil compared to the liquid media. The accumulation of atrazine in actinomycetes, fungi

TABLE 6. CONCENTRATIONS AND BIOACCUMULATION RATIOS (BR) OF ATRAZINE IN FISH, SNAILS AND ALGAE *† (55)

Species	Day	ppb	BR
Fish	9	197	17
	18	186	16
Snails	18	98	8
Algae	18	105	9

[*] Determined in a model aquatic ecosystem. Bottom soil was initially treated with 0.82 ppm atrazine.

[†] BR ratios agree with those reported by Isensee.

and other organisms growing in soils with high levels of atrazine would suggest that in the enviornment such accumulation may serve as a vehicle for the entry of atrazine into certain food chains (55). However, as discussed below, bioaccumulation in higher forms of life is unlikely due to metabolic breakdown of atrazine.

Atrazine is metabolized readily by animals and is considered non-bioaccumulable (7). Very little intact, unmetabolized atrazine is excreted in either the urine or feces of animals. Feeding goats and cows with 1 mg/kg atrazine resulted in transient milk residues which reached a maximum concentration between 8 and 24 hours after feeding, then declined rapidly to the limit of detection within 2 to 4 days (1). The metabolic degradation products of atrazine in animals include hydroxy atrazine, N-dealkylation products (i.e., 2-hydroxy-4-amino-6-ethylamino-atrazine and 4,6-diamino-atrazine), side-chain modified atrazine (i.e., via ω oxidation of the isopropyl group to a carboxylic acid), and glutathione conjugation products (28,1,88,2016). Hydroxy atrazine and N-dealkylation products are rapidly excreted in the urine with no bioaccumulation (1). Moreover, these compounds are nontoxic to mammals, with LD_{50}'s of greater than 5000 mg/kg. The glutathione conjugation product rapidly degrades to the corresponding mercapturic acid which subsequently undergoes mercapturic acid biosynthesis in a path recognized as a general means of detoxification and excretion of numerous foreign compounds in mammals (89), in birds (90) and in insects (91).

5.0 MISCELLANEOUS

As indicated in Section 1.0, commercial wettable power formulations of atrazine contain up to 80% active ingredient and 20% "inerts". None of the inert materials (see Section 1.0) are expected to be very toxic or hazardous.

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Common Name: Dalapon

Chemical Name: 2,2-dichloropropionic acid

Major Trade Names: DOWPON, DOWPON M, DOWPON C, Radapon

Major Applications in Forestry: Site preparation, grass control in seed orchards and seed production areas, release, and vegetation control in established plantations.

SUMMARY

The fate of dalapon in the environment and its potential effect on non-target plants and animals have been the subject of extensive studies. These studies indicate a relatively short environmental persistence and very low-order toxicity to aquatic and terrestrial organisms for dalapon.

Dalapon is absorbed via plant foliage and roots and is apparently not metabolized by plants to any appreciable extent. Residues on plant surfaces decrease very rapidly following application. Microbial degradation is the major contributing factor to the dissipation of dalapon from soil. Degradation rate has been highly variable among the soils studied and has ranged from complete disappearance in less than 2 weeks to two-thirds retention after 8 weeks. The decomposition is more rapid at warm temperatures, in the presence of adequate moisture and at a slightly less than neutral pH. Because of its high water solubility, dalapon is not adsorbed to soil particles to any appreciable degree and is subject to leaching. Field data, however, indicate that under many practical conditions dalapon does not move beyond the first 6-inch depth of soil, probably because microbial degradation proceeds at a faster rate than leaching under field conditions. Chemical degradation, volatilization and photodegradation are not important factors in dissipation of dalapon from soil under field conditions. Although actual data on persistence of dalapon in water are not available, based on laboratory BOD tests and the rapid biodegradation of dalapon in soil, dalapon is expected to undergo rapid biodegradation in the aquatic environment.

Dalapon is fairly selective against annual and perennial grasses and little impact to non-target conifers are expected in forestry applications. Crops susceptible to dalapon damage are also few, and no crop damage would be expected from possible drift due to applications in forest areas. At application rates of 5 to 15 lb/acre used in forestry, birds, fish, other aquatic organisms, honey bees, and soil invertebrates in the spray area should not experience irreversible toxic effects. Based on tests with laboratory animals, dalapon has very low acute mammalian toxicity. Subacute feeding experiments with cattle, sheep, rats and hogs have indicated no mortality and in some cases only minor temporary symptoms. Chronic toxicity tests with dogs and rats have also indicated no effects under conditions tested. Based on results from experiments with rats and birds, normal uses of dalapon are not expected to have adverse impacts on mammalian or avian reproduction. The LC_{50} for dalapon for 12 species of fresh water fish tested is greater than 100 ppm, thus indicating low order toxicity to fish. Dalapon at 50 ppm level has been shown to cause no mortality to fish eggs and fry for several fish species tested. Consistent with its high water solubility, dalapon does not present potential for bioaccumulation in animals. In laboratory tests, residues in the tissues of mammals and birds fed 100 to 1000 ppm dalapon in their diet over periods of weeks, months or years remained below 100 ppm during treatment and soon fell to below one ppm when removed from exposure to dalapon.

Dalapon has essentially no effect on aerobic or anaerobic organisms in soil at dosages approximating commercial usage recommendations. A number of genera and species of algae, fungi, and bacteria tolerate high dosages of dalapon and are capable of decomposing it.

1.0 INTRODUCTION

Dalapon is a moderately selective herbicide for grasses. It was first introduced in 1953 by the Dow Chemical Company and has since gained extensive use for grass control in a wide range of applications including agriculture, industry, right-of-way, and forestry (1,2). In forest applications (primarily in the Northwest), dalapon is used for control of annual and perennial grasses for site preparation, seed orchard and seed production areas, release, and vegetation control in established plantings (2). Despite its general potential uses, dalapon is applied less extensively than other herbicides in forestry. The Dow Chemical Company estimates that, in 1979, dalapon was applied to 4,167 acres or about 0.013 percent of the total forest acres (3).

Dalapon is formulated as the sodium and magnesium salts (4). DOWPON M, a mixture containing 72.5 percent sodium salt and 12.0 percent magnesium salt of dalapon, is the major dalapon formulation and appears to be the only formulation used in forestry applications (2,4). Recommended application rates in forest uses range from 3 to 15 lbs of DOWPON M per acre. Depending on the specific target species and whether broadleaf weeds are also to be controlled, dalapon may be applied along with atrazine, Esteron-99 (2,4-D), or a surfactant (2,5). Dalapon is applied either by ground or aerial spray (2,5).

Data on the amount of dalapon used is very limited. The amount of dalapon used in Forest Service Regions 5 and 6 and by the Bureau of Land Management in Oregon in the past several years are given in Tables 1, 2, and 3.

TABLE 1. DALAPON USE IN FOREST SERVICE REGION 5 (5)

Year	Pounds Applied	Acres Treated	Purpose
1976	25	2	plantation weed control
1976	6252	744	site preparation
1977	56	414	conifer release
1978	1267	344	perennial grass control
1979	3800	997	conifer release
1979	2912	391	site preparation
1979	42	8	grass control

TABLE 2. DALAPON USE IN FOREST SERVICE REGION 6 (5)

Year	Pounds Applied	Acres Treated	Purpose
1975	637	745	timber management
1975	850	93	seed orchard
1976	1	0.5	release
1976	169	30	site preparation
1977	942	230	site preparation
1977	60*	15	release
1978	40	5.25	site preparation
1978	138	262	release
1979	2208	1220	site preparation
1979	32*	4	site preparation
1979	12	3	release

*Dalapon + atrazine applied.

TABLE 3. DALAPON USE BY THE BLM IN OREGON (5)

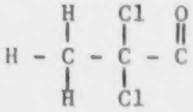
Year	Pounds Applied	Acres Treated	Purpose
1978	none	none	site preparation
1979	1750	804	site preparation
1979	1000	200	site preparation
1979	2160*	540	site preparation
1979	9†	145/60 mi.	road maintenance

*Dalapon + atrazine applied.

†2 lb dalapon + 7 lb 2,4-D applied.

Dalapon appears to cause leaf chlorosis and abnormal growth responses typical of growth regulators. It also displays pronounced contact toxicity (6).

2.0 PHYSICAL AND CHEMICAL PROPERTIES

The active ingredient in dalapon is 2,2-dichloropropionic acid  $\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}-\overset{O}{\overset{\|}{C}}-OH}$, which is a colorless, odorless liquid with a boiling point of 185 to 190°C. It is reported to be "very soluble" in water, alkali solvents and ethanol, and "soluble" in ether (1).

DOWPON M, the formulation of dalapon used in forestry, is a mixture of sodium (72.5 percent) and magnesium (12.0 percent) salts of dalapon. It is an off-white powder which is very soluble in water and most organic solvents. The solubility in water containing 100 ppm hardness is 110 g/100 ml at 22°C (1).

The sodium salt of dalapon has been shown to hydrolyze slowly in water to produce pyruvic acid, and the rate of hydrolysis increased with increasing temperature. After 175 hours, the extent of hydrolysis at 25°C for 1 percent, 5 percent and 18 percent dalapon solutions were 0.41 percent, 0.61 percent, and 0.8 percent, respectively (7).

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM BY PLANTS AND RESIDUES ON PLANT FOLIAGE

Nearly all studies of uptake and metabolism of dalapon by plants have been in connection with crop production. These studies indicate that dalapon can be absorbed by either the roots or foliage. Once absorbed it is translocated throughout the plant. Based on tests with corn, soybean, sugarbeets, barley, sorghum and wheat (6,8), accumulation appears to be greatest in regions of high metabolic activity (e.g., vegetative buds and fruiting areas). Dalapon does not appear to be metabolized by plants within about 2 weeks following uptake, and whether it is metabolized at all is not clear.

Blanchard, et al. (8) used 2-^{14}C dalapon sodium salt to measure the distribution of dalapon in corn and soybean plants. Soybeans were treated by root application in nutrient solution containing 32 ppm of dalapon for four days and by foliar application and held for three days post-application. Corn was treated by root application in a nutrient solution of 2.5 ppm of dalapon for 11 days. Dalapon tended to concentrate in the young tissues as shown by autoradiograms. Extracts of treated plant tissues showed only a single spot (R_f value) on paper chromatograms, corresponding to that of dalapon. Two plausible breakdown products, pyruvic and lactic acids, have different R_f values and were not found. This is evidence that little or no breakdown of dalapon can be detected in plants from three to 11 days after treatment.

Long-term studies are less clear on whether dalapon is metabolized. Nine to ten weeks after treatment with 2-^{14}C dalapon (through severed petioles), approximately 85-90 percent of the radioactivity was recoverable as dalapon (9). Some dalapon may be slowly degraded and the ^{14}C incorporated metabolically into the plant constituents. Smith and Dyer (10), however, attributed the presence of non-extractable radioactive residues in cotton to occlusion or trapping of chemically unaltered dalapon. Quantitatively, it accounted for only a very small percentage of the applied chemical.

The fate of dalapon in plants was also evaluated by Foy (11) who employed dalapon 2-^{14}C and ^{36}Cl for tracer and metabolic studies in cotton, corn, and wheat. Dalapon was absorbed, translocated, and accumulated in plants principally as the intact molecule or its dissociable salt, and remained unchanged for long periods, especially in dormant or quiescent tissues. Slow metabolic decomposition resulted in some release of ^{36}Cl or incorporation of ^{14}C into other compounds indicating eventual breakdown, possibly an initial dehalogenation followed by normal or modified propionate oxidation. Slowness of metabolism or the stability of dalapon may also be indicated by the presence of "dalapon stimulus" in the third generation of seeds after exposure of the first generation of wheat to pre-plant applications of four pounds of dalapon per acre in the field (11). This was detected by typical plant formative effects of dalapon but not by chemical analysis.

Considerable data have been published on residue of crops and grass following treatment with dalapon. These data indicate a rapid decrease in residue following application. The amount of residue is generally related directly to the application rate, is affected by field conditions, and is a function of plant surface area-to-weight ratio. Plant parts with the largest ratio such as foliage have the highest residues. Thus, it would be expected that residues on seeds, stems, fruits, etc., would be lower than for foliage with the same dosage application (4).

Scholl (12) reported that dalapon residues in seedling alfalfa and birdsfoot trefoil decreased rapidly and appeared to be insignificant eight weeks following treatment. This conclusion was supported by Kenaga (4) who presented a review of the literature and the results of plant residue studies conducted by the Dow Chemical Company. Fertig and Schreiber (13) reported that "early residue studies" on forage legumes, alfalfa, and birdsfoot trefoil showed a maximum of approximately 300 ppm of dalapon following use of a spring application of ten pounds of dalapon per acre to these crops. Getzendaner (14) reported analyses of dalapon residues at intervals of zero, one, two, four, six, and eight weeks after application of eight pounds per acre of DOWPON M (8 lb/A, equals 6 lbs of dalapon per acre). Average residues of the active ingredient, dalapon, per one lb of the commercial formulation, DOWPON, per acre after the above time intervals were 135, 28, 25, 21, 6, and 4 ppm, respectively. The average residues of dalapon per one lb of the active ingredient, dalapon per acre, after the same time intervals were 182, 38, 34, 28, 8, and 5 ppm, respectively.

3.2 FATE IN SOIL

Microbial degradation is by far the most important process affecting the fate of dalapon in soil. Other processes which are of lesser importance are adsorption, leaching and runoff, chemical degradation and volatilization. Based on the light absorption characteristics of aqueous solutions of sodium salts of dalapon, it has been concluded that photodecomposition of dalapon in field applications is improbable (15).

3.2.1 Microbial Degradation

The microbial population in soil is capable of degrading dalapon. The rate of degradation appears to vary with soil type and environmental conditions (e.g., soil moisture, pH and temperature). Day, et al. (16) conducted laboratory studies in which 50 ppm of the sodium salt of dalapon was applied to 43 different California soils. The persistence of dalapon was determined by chemical analysis. The rates of decomposition were found to be highly variable among the soils studied, apparently due to differences in the populations of soil microorganisms capable of decomposing dalapon. Decomposition rates ranged from complete disappearance in less than 2 weeks to two-thirds retention of the added dalapon after 8 weeks. The capacity of the soil to decompose dalapon was essentially random with respect to soil series, texture, cation-exchange capacity, total organic matter, and geographical source.

The persistence of dalapon in soil appears to be related to the application rate, temperature, moisture content, pH and soil organic content. At low application rates, phytotoxic concentrations of dalapon have been shown to disappear from soil within 2-4 weeks (17,18,19). At high rates of application, dalapon can persist for several months (18). Southwick (20) reported that, under greenhouse conditions with heavily watered soil, the toxicity of 40 lb/A of dalapon persisted for 8 to 12 weeks. Brown (21) reported that 40 lb/A of dalapon applied in June was still toxic to alfalfa and sweet clover one year later under field conditions. Wingfield, et al. (22) studied the effect of temperature on dalapon disappearance from soil and reported that dalapon disappearance was more rapid at room temperature (19 ± 2°C) than at 2 to 10°C. At 19 ± 2°C, 50 percent of dalapon applied at a rate of 40 kg/ha to the surface of an undisturbed column of undisturbed sandy loam disappeared in about 11 days. Laboratory studies by Theigs (23) indicated that dalapon decomposition was most rapid in warm, moist soil but was very slow in moist soil at 40°F and dry soil at 100°F. Jensen (24) observed that dalapon was decomposed only feebly at pH levels below 5. Kaufman (25) found with five soils in greenhouse and laboratory studies that dalapon degradation by effective microorganisms was affected by organic matter level, pH, cation-exchange capacity, and aeration. Corbin and Upchurch (26) reported that dalapon was almost 100 percent detoxified within a two-week incubation period when high-organic-matter soils were buffered to pH 6.5. Soils buffered to pH 6.5 provided optimum conditions for microbial adaptation and herbicide degradation. Inactivation rate was slower at pH 7.5 and 5.3 and negative detoxication occurred at pH 4.3. Dalapon phytotoxicity in high organic soils increased as pH decreased and reached a maximum at pH 4.3; a change of one pH unit decreased the phytotoxicity (27).

The biological nature of dalapon degradation in soil has been well established. Thiegs (23) compared the rates of degradation of dalapon in autoclaved and non-autoclaved soils. The concentration of dalapon (59 ppm) in the autoclaved soil did not change after incubation at 100°F for one week while in the unsterilized soil, dalapon disappeared in four to five weeks after one application and in one week after the second application of 50 ppm. Based on the observations that dalapon decomposition is adversely affected by low soil moisture, low pH, temperatures below 20°-25°C, and large additions of organic matter, Holstun and Loomis (28) concluded that it was a function of microbiological activity.

A wide range of microorganisms are effective in degrading dalapon. Hirsch and Alexander (29) isolated and characterized strains of Pseudomonas and five strains of Nocardia which decomposed dalapon, liberating 90-100 percent of the halogen within three weeks. Other workers have reported additional species of bacteria, fungi, and actinomycetes that have decomposed chlorinated aliphatic acids. For example, Magee and Colmer (30) reported Agrobacterium, Thiegs (31) reported Flavobacterium, and Jensen (32, 33) added Penicillium, Trichoderma, Clonostachys, and Arthrobacter.

Kaufman (34) found that the microbiological degradation of dalapon was inhibited in the presence of amitrole. Phytotoxic residues of the herbicide persisted longer in the soils when the herbicides were applied in combination than when each was used individually.

3.2.2 Adsorption, Leaching and Runoff

Laboratory studies have indicated that dalapon adsorption to soil particles is very limited. This, which is consistent with the high solubility of dalapon in water, suggests that dalapon is potentially a highly mobile compound. The much more limited mobility observed in field studies appears to be due to microbial degradation proceeding faster than leaching.

Newman and Downing (35) measured the adsorption of herbicide by ascertaining the amount of compound required to cause 90 percent inhibition of crabgrass growth in silica sand, a fine sandy soil, a silt loam, a new muck, and an old muck. Adsorption was considered to result in inactivation and, hence, unavailability of the active ingredient to exert its phytotoxic effect. There was little adsorption of dalapon by any of the soils. (For other herbicides which were strongly adsorbed, 24 to 90 times as much was required to cause 90 percent inhibition in old muck as in silica sand.)

Holstun and Loomis (28) used soil columns to investigate the leachability of dalapon. Preliminary experiments found that 24 lb/A of dalapon was completely leached from the surface inch of three different soils by as little as 2 inches of water. Subsequent experiments evaluating the effects on leaching of sand or organic material additions to the soils also indicated little adsorption of dalapon by any of the three soil types. The addition of sand increased the downward movement of dalapon, but the effect was slight. The addition of organic matter did not appear to affect the location of the maximum dalapon concentration, but did increase the quantity retained in the upper 2 inches of the soil. Smith, et al. (36) studied the leaching of dalapon-^{14}C at the dosage of one lb/A through an 8.5 inch deep soil column of Kawkawlin sandy loam. Nine acre-inches of water applied at one-half inch increments for wetting accounted for the leaching of 99.4 percent of the dalapon in the effluent from the soil column.

Dalapon adsorption and mobility in soil have been compared with a number of other pesticides. Warren (37) compared the leachability of dalapon sodium salt (applied at 8 lb/A) in four soil types with that of several other herbicides. Dalapon and trichloroacetic acid (TCA) were the only herbicides to move readily in all soils tested. Bioassays on crabgrass were used to measure activity. Helling (38) classified 40 pesticides into 5 groups based on relative mobilities on silty clay loam plates, using soil thin layer chromatography based on R_f values. Only four compounds were classified in the group of greatest mobility (least adsorption): TCA, dicamba, amiben, and dalapon. Such materials are among the most likely to leach through or run off soil among the 40 pesticides tested (4).

Even though the laboratory studies indicate that dalapon is a highly mobile compound and should be readily leachable from soils, field data show that under many practical conditions dalapon does not move beyond the first six-inch depth of soil. This is probably because microbial action proceeds at a faster rate than leaching under favorable conditions (4). Kenaga (4) reviewed the literature on dalapon and noted that many of the laboratory studies (including those mentioned above) have often used "exaggerated" conditions of rainfall or soil permeability. Miller and Getzendaner (39) analyzed field soil samples taken from various locations in the United States representing different climates, rainfall, soil types, and soil depths. Samples were taken at intervals of several days to one year after application of DOWPON M or DOWPON grass killers at rates of 4 to 41 lbs/A. No residues of dalapon were found in the zero-to-six inch layer of soil from any treatment after 40 days. In a Wayside, Mississippi soil treatment using 10 lbs of DOWPON/A, the residues of dalapon in the zero-to-six inch layer at 7 days were 2.0 to 2.2 ppm, at 14 days 0.11 to 0.28 ppm, at 28 days 0.06 to 0.15 ppm, and at 42 days <0.025 ppm. No residues of dalapon were found in the 6-to-12 inch layer of soil from any treatment or time interval from application. It was concluded that dalapon is unstable in soil under conditions favorable for microbial growth and thus, it will usually be degraded before appreciable leaching can take place. This conclusion is consistent with laboratory data presented by Kearney, et al. (15) which indicates that physical interactions between soil particles and dalapon are relatively unimportant.

It would, however, be possible for leaching of dalapon to occur if irrigation or rainwater is applied to a site following dalapon application and before substantial biodegradation occurs. Frank, et al. (40) studied the concentrations of dalapon in irrigation water following canal bank applications of 6.7 to 20 lb/A. Maximum concentrations of dalapon found were 0.023 and 0.365 ppm when sampled in the treated area within 30 minutes after application. The treated irrigation canals varied in water flow from 3.4 to 390 cu. ft/second and 0.96 to 2.4 ft/second (2.4 ft/second = 3.65 mph). After several hours only very low levels of dalapon (<10 ppb) were present in waters flowing from the treated area. It should be noted that the highest concentration of dalapon found in the irrigation water (0.365 ppm) would deposit only 0.09 lb of herbicide per acre-inch of water and would be too low a rate to be likely to injure irrigated crops (4) (see Section 4).

3.2.3 Chemical Degradation

Although dalapon is subject to hydrolysis, under field conditions chemical degradation is considered to be very slow and is unlikely to be an important factor in the dissipation of dalapon from soil. Smith, et al. (41) and Brust (7) demonstrated that dalapon and its sodium salt can undergo hydrolysis to pyruvate and HCl. Other investigations have shown that hydrolysis is more rapid under alkaline pH and at elevated temperatures. Smith, et al. (41) isolated sodium pyruvate in essentially quantitative yield after hydrolyzing a dalapon solution containing excess sodium bicarbonate at 110°C for 15 minutes. Brust (7) observed that dalapon sodium salt was hydrolyzed only slowly at 25°C in either dilute (1 percent) or concentrated (18 percent) solutions. At 50°C, the rate of hydrolysis was more rapid, with approximately 25 percent hydrolysis in 8 days at initial concentrations ranging from 1 to 18 percent in water (7).

Hydrolysis of solutions of either dalapon or dalapon sodium salt are accelerated at alkaline pH values. For example, hydrolysis of dalapon sodium salt at 60°C was 20 percent complete in 30 hours at which time the equilibrium pH was 2.3. In contrast, hydrolysis was 40 percent complete in 30 hours when the pH was maintained at 12 during the experiment (42).

Based on reaction rate studies, Kenaga (4) concluded that both dalapon salt and dalapon would have chemical hydrolysis half-lives of several months at temperatures less than 25°C and at initial solution concentrations of less than one percent. Considering the more rapid rate of microbial degradation, Kenaga (4) concluded that it does not appear that chemical hydrolysis of dalapon is a particularly significant degradative pathway in soils.

3.2.4 Volatilization

Volatilization of dalapon salts used in forestry under field conditions is expected to be insignificant. In general, volatilization is primarily a function of temperature and air movement. The vaporization from soil is also dependent on a substance's chemical form and the extent of its interactions with the soil particles (15). As was previously discussed, there is little interaction between dalapon and soil particles. Any volatilization of dalapon at a given temperature would then depend primarily on air movement and the specific chemical form of dalapon. Day (43) and Day, et al. (16) found that some esters of dalapon were more volatile and others less volatile than the acid form. In addition, Foy (44) found that at room temperature, dalapon acid volatilized rapidly from an aluminum surface, whereas only negligible amounts of the sodium salt form disappeared in 64 hours. Kutschinski (45) reported that under more severe temperature conditions (63°C), 69 percent of dalapon applied as the acid to sand disappeared in 6 hours. In comparison, Kutschinski also applied the sodium salt of dalapon to several moist soils, also at 63°C, and found that the greatest loss (from silica sand) amounted to 13.5 percent in 6 hours.

It appears that, when applied to soil, the sodium salt of dalapon will remain in the relatively non-volatile salt form and will not be converted to the more volatile acid form. This has been suggested by Kutschinski (45) who measured dalapon volatility in experiments in which sodium salt of dalapon was applied to moist soils at 63°C. On the basis of the results, Kutschinski concluded that dalapon hydrolyzed to pyruvate and that the liberated H^+Cl^- caused the formation of the acid of dalapon from the applied sodium salt. However, conditions favoring formation of the dalapon acid would not likely occur in most natural soil conditions. This is because the pKa of dalapon acid is low (1.71) and because most soils have some buffering capacity which will remove free protons generated by pyruvate formation. The dalapon acid is only likely to form: (a) in sands where the buffering capacity is low or nil, and (b) in microareas surrounding concentrated centers of dalapon in soils where the buffering capacity would be exceeded (15).

Kearney, et al. (15) comment that while Kutschinski's conclusions appear to be valid, the possibility that the sodium salt of dalapon might also have volatilized under the conditions of his experiment which were extreme compared to natural conditions, cannot be eliminated since the analytical methodology could not have probably distinguished between the acid and salt of dalapon trapped in the gas scrubber used.

In summary, the available data indicate that while some volatilization of the dalapon acid from soils can be expected, very little volatilization of the dalapon salt can occur under normal forest use conditions.

3.3 FATE IN WATER

Actual field data on persistence of dalapon in water appear to be limited to the observations by Frank, et al. (40) who reported negligible concentrations of dalapon in water downstream of a treatment site after the water had travelled a distance of 32.2-40.2 km. Based on the laboratory BOD test results and the observation of the rapid degradation of dalapon in soil by microorganisms, dalapon is expected to biodegrade readily in the aquatic environment. Kenaga (4) reported that the BOD/COD ratios for DOWPON M and dalapon sodium salt (at 3.33 and 1.67 ppm concentrations) are comparable to those for such readily biodegradable substances as sucrose, ethanol, and glutamic acid.

Because of its high water solubility and lack of affinity for soil particles, appreciable adsorption of dalapon on suspended or bottom sediments is not expected in natural waters. Based on the discussion in the preceding sections, chemical degradation and volatilization probably occur too slowly to account for substantial loss of dalapon from water. Aquarium studies conducted by Smith, et al. (36) provide further evidence that volatility is not a route for significant loss of dalapon from water.

4.0 IMPACTS ON NON-TARGET ORGANISMS

4.1 PLANTS

Dalapon is relatively selective against annual and perennial grasses (6). This selectivity has been attributed to possible differences in the metabolism between target and non-target species (46). In forest site preparation applications, dalapon is used at least two weeks before planting conifers. Tests run by Stewart and Beebe (47) in Wenatchee National Forest indicated that 5 lb of dalapon per acre could provide adequate grass control without damaging ponderosa pine seedlings planted immediately after spraying. Conifer damage may result, however, when dalapon is used in conjunction with certain other herbicides. In at least one area in southwestern Oregon, a combination of atrazine and dalapon resulted in complete defoliation of well-established ponderosa pines 8 to 15 feet tall (48). No information on the amount of the mixture applied or the mix ratio in this incident was reported, but it appears that there is a synergistic effect when these two chemicals are used in combination which increases their activity and effect upon conifers (48).

Crops susceptible to dalapon damage are few and, in general, no crop damage would be expected from possible drift due to applications in forest areas. Dalapon is used for grass control on several agricultural crops including sugarcane, sugarbeets, corn, potatoes, asparagus, grapes, flax, new legume spring seedlings, citrus, and deciduous fruit, coffee, certain stone fruits and nut trees (1). Cotton is considered to be tolerant to dalapon while sorghum is considered susceptible (6).

Foy and Miller (49) investigated the effect of dalapon on maturity, yield, and seed and fiber properties of cotton by applying a basally directed spray of dalapon during the early square and full flowering stages of development as well as after a full boll load had developed. Application rates of 3 and 6 pounds per acre during the two flowering stages caused significant delay of maturity and reduction of cotton yield, with the high rate being more severe. Later applications did not produce any observed deleterious effects at either rate. Germination of seed from treated cotton was measurably retarded (at 48 and 96 hours) but final viability was not reduced. The effect of retarded germination also was observed in seeds germinated after two years in storage. Foy and Miller (49) also reported that the influence on germination was correlated with dosage and with the time of application in relation to reproductive development.

To prevent depression of crop yield, Newton and Norgren (50) recommended an allowable level of 0.02 mg/l of dalapon in sources of irrigation water and a maximum of 0.1 mg/l in smaller streams where maximum concentrations tend to exist only briefly and would not lead to a harmful accumulation of dalapon on the crop.

4.2 FAUNA

At application rates of 5 to 15 lb/acre recommended for forestry uses, it appears that birds, fish, other aquatic organisms, honey bees, and soil invertebrates will not be exposed to levels of dalapon which cause observable toxic effects. Under worst-case conditions (e.g., treatment of a large area at maximum recommended application rate and no rainfall), it appears possible that a small browsing mammal (e.g., a rabbit) could consume enough dalapon to cause an acute toxic reaction. One study, however, indicated that larger mammals (calves and sheep) grazing on dalapon-treated feed did not suffer visible harmful effects (51).

Kenaga (4) has reviewed the literature on the toxic effects of dalapon on mammals, birds, fish and other aquatic animals, honey bees, and soil invertebrates. This section, with only minor modifications, is extracted from his review.

4.2.1 Effects on Mammals

Some LD_{50}'s reported for dalapon sodium salt and two dalapon formulations are presented in Table 4. The high LD_{50} value indicates very low acute toxicity to mammals.

Table 5 presents the results of subacute toxicity experiments with cattle and sheep. The animals were dosed with daily oral capsule or drench applications of dalapon sodium salt at rates of 15 to 500 mg/kg/day, equivalent to an intake of about 150 to 1,500 ppm in the diet; no mortality occurred at any of the dosage rates which were given for from 9 to 481

TABLE 4. ACUTE ORAL TOXICITIES OF DALAPON TO MAMMALS (4)

Species	Sex	LD_{50} (mg/kg)		
		Dalapon sodium salt	DOWPON[*]	DOWPON M[+]
Rat	M	9,300	5.660	5,660
	F	7,570	5,660	5,660
Mouse	F	>4,600	--	--
Guinea pig	F	3,860	4,930	2,830
Rabbit	F	3,860	2,830	2,140

[*] Formulation containing 85 percent dalapon sodium salt.

[+] Formulation containing 72.5 percent dalapon sodium salt and 12 percent dalapon magnesium salt.

TABLE 5. TOXICITY OF DALAPON SODIUM SALT TO CATTLE AND SHEEP (4)

No. days treated	Means of oral dosing	Dosage (mg/kg/day)	Effects
Cattle			
10	Drench	250	None
9	Drench	500	Throat irritation
10	Capsure	500	None
Sheep			
10	Drench	50	None
10	Drench	100	None
10	Capsule	100	Ill but survived, 6% wt loss
481	Capsule	100	None, 10% wt loss after 80 treatments
10	Drench	250	None
10	Drench	500	Ill but survived, 17% wt loss
10	Capsule	500	Ill after 7 treatments but survived, 6% wt loss

successive days. Cattle exhibited some throat irritation at 500 mg/kg with an oral drench and sheep lost some weight at as low as 100 mg/kg/day when fed for 10 days. In another study, Paynter, et al. (52) reported the treatment of a heifer and a bull suckling calf with 1,000 mg/kg/day for 10 successive days. Some symptoms exhibited were temporary. No mortality occurred. Macroscopic and microscopic examination of tissues from the animals sacrificed on the eleventh day revealed these tissues to be within normal limits, with the possible exception of kidney tissues of the bull.

Paynter, et al. (52) also conducted a 97-day dietary feeding study on rats using diets containing 115, 346, 1150, 3460, and 11,500 ppm. No mortality occurred at any of these dosages. There was no measured effect on male rats at 1150 ppm (= 115 mg/kg/day) and on female rats at 115 ppm as judged by food consumption, average body and organ weights, and by hematological, gross, and histopathological examinations.

Goldstein and Long (51) conducted field tests with dalapon (sodium salt?) on a grassy pasture using 30 lb/100 gal of water (= approx. 30 lb/A). Two calves grazed on the pasture until the vegetation turned brown, with no visible harmful effects to the calves. Oats treated with 2.5, 5, 10, and 20 lb/100 gal (= approx. same rates/A) were fed on by calves and sheep without ill effects. Sudan grass treated with 20 lb/100 gal was fed upon by a calf without ill effect. Goldstein and Long (51) added dalapon sodium salt at the rate of "a pint of the standard concentration of dalapon spray per five gallons of drinking water" (probably equivalent to 12,500 ppm); this was the drinking source for a hog, sheep, and cattle for two weeks without causing visible ill effects.

Chronic toxicity tests in which dogs were administered capsules daily, 5 days a week for 52 weeks, containing doses of 15, 50, or 100 mg/kg/day of dalapon sodium salt were conducted by Paynter, et al. (52). The usual extensive toxicological parameters measured indicated no effect from these treatments except increases in average kidney weights at 100 mg/kg/day. In a 2-year dietary feeding test with rats, also conducted by Paynter, et al. (52), rats consumed diets containing 100, 300, and 1,000 ppm of dalapon sodium salt for 2 years, equivalent to 5, 15, and 50 mg of dalapon sodium salt/kg/day, respectively. The usual extensive toxicological parameters measured during chronic feeding tests indicated no effect from these treatments except increases in average kidney weights at 50 mg/kg/day.

The effect of dalapon on mammalian reproduction has been investigated by a number of investigators. In studies by Paynter, et al. (52), young rats were fed for at least 110 days on diets containing 300, 1,000, or 3,000 ppm of dalapon sodium salt (= about 30, 100, or 300 mg of dalapon sodium salt/kg/day) continuously through each of three generations of two litters each, with no effect on reproduction (fertility, gestation, viability) and lactation. No adverse effect was seen on body weight, a favorable indicator of normal growth and maturation. Thompson, et al. (53) administered dalapon by gavage to pregnant rats from day 6 through 15 of the gestation in a tolerance study designed to suggest dose levels acceptable for teratogenic studies. Dosages given were 250, 500, 1,000, 1,500, or 2,000 mg/kg/day. The following parameters were examined: maternal body weights and gains, food consumption, number of viable fetuses, fetus resorptions, and corpora lutea, individual pup weights and sex, and gross external examination of pups. As the result of these tests, only the following notable observations were made: clinical signs of toxicity consisted of soft stools and slight appetite depression in dams from the 2,000 mg/kg dosage group. One rat from the 1,500 mg/kg group had diarrhea. Weight gains for pregnant dams were lower than controls at 1,500 or 2,000 mg/kg/day. Fetal resorption rate was increased at both the 1,500 and 2,000 mg/kg dosage levels but the increase was not significantly different from controls. Pup weights from the 2,000 mg/kg dosage level were significantly lower than controls. No effects were seen at 1,000, 500, or 250 mg/kg/day.

Teratological studies of dalapon in the rat were reported by Emerson, et al. (54). Dalapon was administered in distilled water once daily, by gavage, from day 6 through 15 of gestation (sperm positive vaginal smear = day zero). Four groups of mated females were administered 0, 500, 1,000, or 1,500 mg of dalapon/kg/day, respectively. They were killed on gestation day 20 and fetuses were removed by caesarean section. The following tests were conducted: clinical observations, maternal body weights on days 0, 6, 15, and 20, food consumption on days 6, 15, and 20, observations on the number of viable fetuses, resorptions, and corpora lutea, individual fetal weights and sex, external examination, and skeletal (two-thirds) and visceral (one-third) examinations.

All rats treated with dalapon were restless for approximately 10 minutes following dosing. Focal alopecia, intermittent staining of rear quarters with urine, and soft stools were observed in some treated rats. Mean weight gains and food consumption for dalapon-treated adult rats during the test interval (days 0 to 20) did not differ significantly from the controls. However, mean weight gains (500 and 1,500 mg/kg/day groups) and mean daily food consumption (1,500 mg/kg/day group) were significantly less than the controls for the dalapon treatment interval (gestation period, days 6 to 15). Mean pup weights were significantly less than controls only in groups given 1,000 or 1,500 mg/kg/day. An increased incidence of minor variants such as retarded ossification of sternebrae was observed in fetuses of treated dams and was associated with decreased fetal weights. Spontaneous major visceral abnormalities consisted of unilateral microphthalmia in one fetus each of the 500 and 1,000 mg/kg/day groups.

Kenaga (4) stated in summary that no major dose-related skeletal or visceral abnormalities were observed in the fetuses of dams treated with dalapon and, other than reduced pup weights in the 1,000 and 1,500 mg/kg/day treatment levels, no untoward effects were detected.

4.2.2 Effects on Birds

Based on reported bioassay results, normal uses of dalapon should present no adverse impacts on birds and beneficial insects such as bees. The acute oral LD_{50} of dalapon sodium salt to chickens is reported at 5,600 mg/kg (52). Palmer and Radeleff (55) reported that chickens treated with 10 daily repeated oral treatments using capsules containing 500 mg dalapon sodium salt/kg/day suffered no mortality and only slight weight-gain reductions (30 percent vs. 42 percent) over untreated chickens. No mortality or weight loss occurred under the same test conditions with dosages of 100 mg/kg/day.

Table 6 presents the reported results for acute and subacute dietary feeding studies on several species of wild birds. Pheasants, Japanese quail, and mallards fed 5,000 ppm of dalapon sodium salt for 5 days suffered no mortality. Pheasant, bobwhite, and mallard populations fed 1,000 to 5,000

TABLE 6. TOXIC EFFECTS OF DALAPON IN DIET OF VARIOUS WILD BIRD SPECIES (4)

Species	Age	Amount in diet (ppm)	Test period (days)	Mor-tality %	Toxicant consumed (mg/kg/day)
Pheasant	Young	5,000	169	24	431
	Adult	5,000	10	10	250
	Adult	5,000	24	90	-
	2-3 wk	5,000*	5	0	-
Japanese quail	2-3 wk	5,000*	5	0	-
Bobwhite	Young	5,000	100	40	-
	Adult	5,000	100	95	610
Mallards	Young	5,000	100	24	-
	Young	1,000	100	68	-
	Adult	2,500	100	85	230
	Adult	1,000	100	94	120
	2-3 wk	5,000*	5	0	-

*Dalapon sodium salt.

ppm of dalapon for various periods (10 to 169 days) sustained partial but not 100 percent mortality. Mallards appeared to be the most sensitive species tested.

The potential effects of dalapon on bird reproduction have been evaluated by dalapon injection into eggs and in dietary feeding tests. The effects of dalapon when injected into eggs represents a severe test, both because of the mechanical and physiological effects of injecting chemicals through the shell and because the egg has no external excretory way to dispose of unmetabolized compounds. Dunachie and Fletcher (56,57) injected from 10 to 500 ppm of dalapon by weight of egg via an acetone solution into hens eggs. No teratogenic effects were seen at 500 ppm, the highest dosage tested. Hatchability of eggs was unchanged in treatments at or below 200 ppm and was 63 percent and 70 percent of control at 300, 400, and 500 ppm levels, respectively.

Dietary feeding reproduction tests conducted on adult pheasants, bobwhites, and mallards are shown in Table 7. The highest dosages used (1,000 to 5,000 ppm in the diet) were checked for effects on the hatching success in terms of chicks per hen. The dosages selected were the highest of those used in Table 6 for each species and resulted in high adult mortality. Presumably, part of the adult mortality occurred after the reproduction tests were finished. In any case, the dosages were in the partially lethal range for adults. In spite of these high dosages, reproduction was not decreased in treated bobwhites and only partially with pheasants and mallards. Effects on reproduction were those related to number of eggs laid, a common effect at sublethal dosage levels. There was no effect on the viability and fertility (hatching success) of the three species compared to the controls (4).

TABLE 7. EFFECTS OF DALAPON SODIUM SALT ON REPRODUCTION OF THE MALLARD, PHEASANT, AND BOBWHITE (4)

Species	Dalapon Sodium Salt (ppm)	Eggs/Female			Viable Young Per Female[*]			% Viable Young Per Egg[†] Laid	
		Control (A)	Test (B)	% Control/Test (B/A)	Control (C)	Test (D)	% Control Test (D/C)	Control (C/A)	Test (D/B)
Mallard	2,500	27	6.8	25	5.1	2.6	51	19	38
	1,000	21	11	51	11	4.7	43	53	45
Ring-necked Pheasant	5,000	32	22	68	12	6.3	55	36	29
Bobwhite	5,000	67	82	122	33	42	128	49	51

[*] Chicks per hen.

[†] Hatching success.

4.2.3 Toxicity to Honey Bees

Research on the toxicity of herbicides to honey bees indicates that the toxicity depends on the chemical, the formulation, and the carrier used with the herbicide. In addition, the method of testing seems to have an important influence on the outcome of the test. Toxicants can kill honey bees by acting as stomach poisons, as contact poisons, and in the case of herbicides, through destruction of the food source. The toxicity of dalapon to honey bees has been studied as both a contact poison and a stomach poison.

Dalapon is considered to be relatively non-toxic to honey bees (58). Laboratory tests at the Dow Chemical Company showed that honey bees immersed and wetted momentarily in dalapon sodium salt solution at a concentration of 20,000 ppm experienced no mortality 24 hours after immersion (4). Anderson and Atkins (59) classified 163 pesticides into three groups on the basis of field tests and commercial experiences for the more commonly used materials. Laboratory contact data (LD_{50} values) from Atkins and Anderson (59) were also used as follows: highly toxic <2 μg/bee, moderately toxic 2 to 10 μg/bee, and relatively non-toxic >10 μg/bee. Dalapon was classified in the relatively non-toxic group by these researchers who characterize substances in this category as those that "can be used around bees with a minimum of injury" (62). Duval (60) made a similar evaluation of toxicity of pesticides to honey bees, classifying dalapon as relatively non-hazardous among the many pesticides evaluated. According to Kenaga (4), the available data on impact of dalapon on bees are in overwhelming contradiction to the statement by King (61) (reportedly made without supportive data) that dalapon should not be used in areas of high bee activity because of severe contact toxicity.

The potency of dalapon as a stomach poison was investigated by Morton, et al. (58) who fed bees 60 percent sucrose solutions containing 0, 10, 100, and 1000 ppmw dalapon. As a measure of toxicity, the investigators compared the number of days required for half of the bees to die (half-life) in a group of bees fed dalapon to that for a control group. All bees tested were newly emerged adults less than 24 hours old. Significant reductions in the half-life of the groups fed 10 and 100 ppmw concentrations of dalapon were not observed. The group fed dalapon at 1000 ppmw did have a slightly shorter half-life than the control group (37.0 vs. 51.8 days).

4.2.4 Effects on Fish and Other Aquatic Organisms

Various studies have been reported on the acute toxicity of various dalapon formulations to several species of fish under a range of temperature and exposure durations. The reported results, as summarized by Kenaga (4), are presented in Table 8 for dalapon sodium and magnesium salts for 12 species of fresh water fish in static water. As noted in the table, the LC_{50}

for all species is greater than 100 ppm of dalapon, which represents a low order of toxicity. An acute toxicity test with dalapon in flowing water has also showed a similar low order of toxicity to large-mouth bass (63).

TABLE 8. TOXICITY OF DALAPON AND FORMULATIONS TO FISH (4)

Species	Water temp.	Exposure (hours)	Material tested[a]	Concentration (ppm)		Mortality (%)
				Formulation[b]	Dalapon	
Rainbow trout	12°C	96	Tech.	>100(Na)	>87	50[h]
	20°C	24	DOWPON	340F	252[g]	50
	20°F	48	DOWPON	210F	155[g]	50
	50°F	24	DOWPON S	430F	318	50
	50°F	96	DOWPON S	430F	318	50
	50°F	96	DOWPON S	300F	222	0
Brown trout	50°F	24	DOWPON S	345F	255	50
	50°F	96	DOWPON S	345F	255	50
	50°F	96	DOWPON S	300F	222	0
	50°F	72	DOWPON S	500F	370	100
Coho salmon	68°F	24	DOWPON S	340(Na)	295	50
	68°F	48	DOWPON S	310(Na)	295	50
	68°F	72	DOWPON S	325(Na)	282	50
	68°F	96	DOWPON S	310(Na)	269	50
Bluegill	12°C	96	Tech.	>100(Na)	>87	50
	12°C	7 Days	Tech.	—	80	0
	12°C	15–21 Days	Tech.	—	50	0
	25°C[d]	24	RADAPON	480(Na)	416	50
	25°C[d]	48	RADAPON	440(Na)	381	50
	25°C[d]	96	RADAPON	440(Na)	381	50
	25°C[e]	24	RADAPON	510(Na)	442	50
	25°C[e]	48	RADAPON	440(Na)	381	50
	25°C[e]	96	RADAPON	290(Na)	251	50
	75°F	24	RADAPON	—	115[g]	50
	75°F	48	RADAPON	—	115[g]	50
	75°F	96	RADAPON	—	105[g]	50
Yellow perch	75°F	72	DOWPON S	300F	222	0
	75°F	72	DOWPON S	400F	296	100
Pumpkinseed	75°F	72	DOWPON S	300F	222	0
	75°F	72	DOWPON S	400F	296	0
	75°F	72	DOWPON S	500F	370	75
Largemouth bass	68°F	48	DOWPON	1,000(Na)	867	0
	68°F[f]	168	DOWPON	1,000(Na)	867	100
	68°F[f]	168	DOWPON	250(Na)	217	0
Channel catfish	12°C	96	Tech.	>100(Na)	>87	50
Goldfish	12°C	96	Tech.	>100(Na)	>85	50
	80°F	96	DOWPON	—	200	0
	80°F	96	DOWPON M	—	200	0
	83°F	48	Tech.	10(Na)	7	0
Fathead minnow	50°F	24	DOWPON S	480F	355	50
	50°F	48	DOWPON S	430F	318	50
	50°F	72	DOWPON S	410F	303	50
	50°F	96	DOWPON S	315F	255	50
	50°F	96	DOWPON S	200F	148	0
	75°F	72	DOWPON	300F	222	0
	75°F	72	DOWPON	400F	296	50
	75°F	72	DOWPON	500F	370	100
	25°C[d]	24	RADAPON	440(Na)	381	50
	25°C[d]	48	RADAPON	410(Na)	331	50
	25°C[d]	96	RADAPON	300(Na)	338	50
	25°C[e]	24	RADAPON	420(Na)	364	50
	25°C[e]	48	RADAPON	310(Na)	303	50
	25°C[e]	96	RADAPON	290(Na)	251	50
Lake emerald shiner	57°F	72	DOWPON	4,000(Na)	2,960	0
Harlequin	20°C[c]	24	DOWPON	300F	222	50
	20°C[c]	48	DOWPON	240F	178	50

[a] DOWPON and RADAPON are trademarks of the Dow Chemical Company.

[b] *F* = formulation containing salt of dalapon, *Na* = sodium salt of dalapon; concentrations in terms of active ingredient.

[c] Twenty percent replacement of treated water every ten minutes.

[d] Soft.

[e] Hard.

[f] Constant flow of water.

[g] May be as sodium salt.

[h] 50 = LC_{50} value in all cases.

Table 9 presents data on the toxicity of dalapon to fish eggs and fry. In tests with four species of fish, 50 ppm of dalapon caused no mortality to the fry. Green sunfish eggs (embryo) were not affected by 50 ppm of dalapon. Two species of salt water fish (longnose killifish and white mullet) were also tested and found to be very tolerant to dalapon (see Table 10). The substitute toxicity of dalapon to fish has also been evaluated. Lawrence (64,65) tested dalapon at 80 ppm for 7 days and at 50 ppm for 15 to 21 days without causing mortality to bluegills. Folmar (66) reported that rainbow trout (Salmo gairdneri) avoided 1.0 ppm of the dalapon sodium salt.

TABLE 9. TOXICITY OF DALAPON TO FISH EGGS AND FRY*(4)

Species	Exposure (days)	Dalapon (ppm)	Mortality (%)
Bluegill			
Small	12	50	0
Fry	8	50	0
Green sunfish			
Fry	8	50	0
Egg embryo	3	50	0
Lake chubsucker			
Fry	8	50	0
Smallmouth bass			
Fry	8	50	0

*At 22° to 25°C water temperature.

Dalapon sodium salt has been tested on a number of species of insects and other crustaceans, both in fresh water and in salt water in short-exposure tests. Such tests have also been conducted on snails, oysters, and marine phytoplankton (see Tables 10 and 11). The no-effect level of dalapon for snails, dragonflies, stoneflies, and several crustaceans is at least 200 ppm. Daphnids are more sensitive, being "immobilized" at 11 to 16 ppm. Shrimp are "immobilized" 40 percent at 0.9 ppm.

The highest concentrations of chemicals which were tested by Butler (67) (Table 10) in estuaries where shrimp, oysters, and crabs grow, are at low ppm concentrations since even ppb concentrations are not likely to occur after herbicidal use because of dilution.

TABLE 10. THE EFFECT OF DALAPON ON AQUATIC ORGANISMS IN SALT WATER (67)

Organism	Exposure (hours)	Temp ($^{\circ}C$)	Dalapon (ppm)	Effect
Longnose killifish	48	29	37*	0% mortality
	48	20	0.87†	0% mortality
White mullet	48	27	37	0% mortality
Brown shrimp	48	29	0.87	47% immobilization
Blue crab	48	24	37	No effect
Eastern oyster	96	31	0.87	0% mortality or shell-growth effect
Phytoplankton	4	-	0.87	0% decrease in carbon fixation

* Dalapon sodium salt tested.

† Dalapon sodium salt tested as RADAPON herbicide formulation.

TABLE 11. THE EFFECT OF DALAPON ON AQUATIC INVERTEBRATES (4)

Organisms	Exposure (hours)	Temp ($^{\circ}F$)	Dalapon sodium salt (ppm)	Effect
Entomostracans				
Daphnida (Cladocerans)				
Simocephalus serratus	48	60	16	EC$_{50}$†
Daphnia pulex	48	60	11	EC$_{50}$†
Cyclops sp.	24	80	400 (a.e.)*	100% mortality
	24	80	200 (a.e.)*	0% mortality
Eubranchipius sp.	24	80	400 (a.e.)*	100% mortality
	24	80	200 (a.e.)*	0% mortality
Insects				
Stoneflies, _Pleronarcys California_, naiad	96	60	100	None apparent
Dragonfly, _Aeschna_ sp.	48	-	1,600 (a.e.)*	0% mortality
Snails				
Planorbis sp.	-	-	400	50% mortality
	-	-	200	0% mortality
Physa sp.	-	-	400	50% mortality

*a.e. = acid equivalent

†EC$_{50}$ = 50 percent immobilization or mortality

4.2.4 Effects on Soil Invertebrates (Arthropods, Nematodes, and Earthworms)

Fox (68) studied the effect of dalapon sodium salt on the numbers of wireworms, springtails, mites, earthworms, and millipedes in grassland soil over a two-year period after application. Since dalapon destroys grass, populations of invertebrates feeding on grass and succession plants will be affected by the kind of plants remaining. Dalapon at 40 lb/A or 20 lb/A did not affect wireworm populations, principally those of the genus *Agriotes*. A dosage of 20 lb dalapon/A resulted in slightly increased numbers of millipeds and springtails (suborder *Arthropleona*) in the first year and increase in numbers of mites (unspecified) in the first and second year (at the 95 percent confidence limits). No significant increase or decrease in numbers of earthworms (*Lumbricidae*) occurred.

Courtney, et al. (69) found that dalapon applied at 5 lb/A to colonial bentgrass reduced the number of nematodes by 94 percent. On the basis of unpublished data, Edwards, et al. (70) state that dalapon is "not toxic to soil animals".

4.3 BIOACCUMULATION POTENTIAL

Data provided by the manufacturers indicate no potential for dalapon bioaccumulation in mammals, birds, fish, snail or daphnids (4,36). Studies reported by other investigators also indicate that while residue buildup may occur in plants, significant accumulation of a permanent nature in animals is unlikely. The observed low level magnification of dalapon in the aquatic fauna has been attributed to physical adsorption and not to metabolic processes (4). In laboratory tests, residues in the tissues of mammals and birds fed 100 to 1000 ppm of dalapon in their diet over periods of weeks, months, or years remained below 100 ppm during treatment and soon fell to below 1 ppm when removed from exposure to dalapon (4).

Smith, et al. (36) studied the distribution of dalapon sodium salt, in an aquarium containing water with a concentration of 5 ppb of dalapon and fish, snails, Daphnia sp., submerged plants (*Cabomba caroliniana*), floating plants (*Limna minor*), and algae over a three-day exposure period. A second identically furnished aquarium was used except that instead of using live organisms, the plants were killed by autoclaving and the animals were killed by freezing them in Dry Ice prior to putting them in the aquarium. The differences with time between residues from organisms in the two aquariums were essentially that due to adsorption and absorption in the first aquarium minus that due to adsorption in the second aquarium. Concentrations of dalapon in water remained at 5 to 6 ppb throughout the exposures, showing little or no volatility from water or overall adsorption from water by organisms. Fish appeared to contain up to 15 ppb on or in tissues of both dead and live whole fish. Snails and Daphnia sp. contained residues less than that of the surrounding water environment. Duckweed (Limna minor) contained about 40 to 50 ppb when dead and up to about 180 ppb when alive. Cabomba caroliniana contained about 20 to 50 ppb when dead, but around 780 ppb when alive and appeared still to be absorbing residues after 72 hours exposure.

4.4 MICROORGANISMS

Studies conducted on the effect of dalapon on nitrification by soil bacteria indicate that a significant, but temporary, reduction in nitrification would result following application of dalapon at levels recommended for forest use. Reid (71) studied the effect of dalapon sodium salt on nitrification rate as a measure of the changes in soil microflora at 25°C under aerated conditions [nitrifying bacteria are among the most sensitive microorganisms to herbicides (15)]. At concentrations corresponding to dalapon application rates of 25, 50, 100, and 150 lb/A, nitrification rates were 30, 23, 20, and 2 percent of the control, respectively, 14 days after treatment and 95, 80, 77, and 48 percent of the control, respectively, after 28 days. Mayeux and Colmer (72) observed that dalapon at concentrations of up to 700 ppm had little effect on nitrite oxidation.

Several studies have reported the nitrogen fixing Azotobacter to be very resistant to dalapon and other chlorinated aliphatic herbicides (4). For example, Magee and Colmer (73) found that the minimum dalapon concentrations necessary to produce maximum inhibition of respiration of Azotobacter species varied among species from 2,000 to 10,000 ppm. Newman and Downing (35) reported that at normal rates of treatment, dalapon should not have adverse effects on Azotobacter. Little is known about the effect of dalapon on symbiotic nitrogen-fixing bacteria, although Worsham and Giddens (74) have reported that dalapon had no effect on soybean nodulation at application rates of 17, 34, and 68 lb/acre. MacKenzie and Macrae (75) tested the tolerance of the nitrogen-fixing system of Azobacter vinelandii to dalapon sodium salt. The acetylene reduction and the growth rate of the bacterium were not affected by 5 and 50 ppm dalapon sodium salt in the growth media. These concentrations are equal to or in excess of those which would occur from commercial use of dalapon, even when applied directly to water (4).

The effects of dalapon on soil microorganisms other than nitrogen fixing bacteria have been evaluated by a number of investigators. Both stimulatory and inhibitory effects have been observed. In a few instances, initial reductions in growth have been followed by increases in activity. Increases may be due to either adaptation and proliferation of "effective" microorganisms, or to proliferation of organisms resistant to the effects of the herbicide. Magee (76) observed that dalapon stimulated the multiplication of soil bacteria, actinomycetes, and fungi. Worsham and Giddens (74) also observed an increase in numbers of actinomycetes and bacteria present in treated soil. Hale, et al., found that low dalapon concentrations (50-150 ppm) increased oxygen uptake by soil microorganisms, whereas higher concentrations (600 ppm) slightly inhibited oxygen uptake. Elkan, et al. (78,79) observed that sodium propionate greatly increased both respiration and total numbers of soil microorganisms but marketly depressed the numbers of fungi. Stimulation in this case was attributed to higher bacterial counts arising subsequent to inhibition of fungi.

Walsh (80) found the sodium and magnesium salts of dalapon to be 4 to 25 times less toxic on the basis of 10 days growth at 20°C than dalapon to four species of unicellular algae in test tubes containing artificial sea water at a salinity of 30 parts per thousand. Even greater differences (around 100-fold) between the acid and salts occurred in regards to decrease in oxygen production as measured by a photosynthesis respirometer over a 90-minute exposure at 20°C. None of the organisms appeared sensitive to dalapon or its sodium or magnesium salts at concentrations which would be expected to occur in natural marine waters. Venkataraman and Rajyalakshmi (81) found blue-green algae tolerant to dalapon at dosage rates equivalent to 200 kg/ha (179 lb/A) over 15-day period. The species included those in the genera Aulosira (fertilissima), Tolypothrix (tenuis), Anicystis, Anabaena, and Nostoc.

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Common Name: Dicamba

Chemical Name: 3,6-dichloro-o-anisic acid

Major Trade Name: Banvel

Major Applications in Forestry: Dicamba is used primarily for site preparation in southeastern pine forests and in the Pacific Northwest.

SUMMARY

Most of the studies on the fate of dicamba in the environment have been on non-forest systems. There is a limited amount of data available in connection with application to forests.

The degradation of dicamba is favored in soils with a high organic matter and moisture content, and at higher temperatures. Degradation is primarily due to microbial action. Under field conditions, dicamba will probably not persist more than several months in most soils. The products of dicamba degradation in soil are 3,6-dichlorosalicyclic acid and CO_2.

Dicamba has been shown to volatilize from soil and leaf surfaces but the extent and significance of losses due to volatilization have not been determined. Dicamba is considered to be a very mobile herbicide. The dimethylamine salt is extremely water soluble. Studies have shown that salts of dicamba readily leach in soil and that there is very little adsorption of dicamba onto most soil types. Photodecomposition is probably not a major route of degradation.

There are few studies available on the fate and persistence of dicamba in water. Model ecosystem studies indicate that dicamba and its metabolites persist in conjugated or anionic forms in water. It slowly transforms to 5-OH dicamba in water (about 10 percent after 32 days) and is very slowly decarboxylated.

Dicamba is phytotoxic to a variety of plant species, including conifers. Plant susceptibility depends on differences in the distribution of dicamba within a plant and differences in the rate of absorption, translocation, and metabolism. Dicamba has a low level of acute toxicity to mammals and birds. The oral LD_{50} of technical Banvel to rats and mallard ducks is 1707-2900 mg/kg and 2009 mg/kg, respectively. It is more toxic to fish. The 96-hr. LC_{50} is 135 mg/l for bluegills and rainbow trout. Dicamba has been shown to be relatively non-toxic to bees. It does not bioaccumulate.

1.0 INTRODUCTION

Dicamba, 3,6-dichloro-o-anisic acid, was introduced in the early 1960's as a selective herbicide for preemergence and postemergence control of annual broadleaf and grassy weeds in cereals (1). It is currently registered for brush control along rights-of-way and for control of both annual and perennial broadleaf weeds in corn, sorghum, small grains, rangeland, pastures, turf, and noncropland (2). Foliar and soil applications of dicamba can be used to control phenoxy-tolerant broadleaf weeds and brush species (3).

In forestry, dicamba is used primarily for site preparation since it is highly phytotoxic to conifers (4,5,6). It is used to control deciduous shrubs and trees, conifers and forbs (7). In the Pacific Northwest forests, dicamba has been effective in controlling western swordfern (4), chinquapin oak and associated hardwoods, alder, vine maple, and maple stump sprouts (8).

Complete quantitative data on the extent of dicamba use in forestry are not available. Based on a survey of major timber companies, no dicamba was used by these companies in the southwest in 1979. However, USFS has reported some use of dicamba in the southeastern pine forests in 1979 (9). These reported uses are shown in Table 1.

TABLE 1. DICAMBA USE BY THE USFS IN SOUTHEASTERN PINE FORESTS IN FY 1979 (9)

Amount Used	Units Treated	Target Pest/Purpose
11 lbs dicamba (+23 lbs 2,4-D)	23 acres	aquatic weeds
24 lbs dicamba (+48 lbs 2,4-D)	140 acres	thistle control
32 lbs dicamba (+64 lbs 2,4-D)	90 miles (spot treatments)	weed control for right-of-way
675 lbs dicamba (+1350 lbs 2,4-D)	810 acres	site preparation
394 lbs dicamba (+803 lbs 2,4-D)	773 acres	release

The USFS pesticide use report for FY 1976 indicates that only 0.2 lbs of dicamba were used by the USFS in Region 5 (California) to treat 0.3 acres for release (10). No dicamba use was reported for FY 1977, 1978, or 1979. In Region 6 (Oregon and Washington) (10), USFS pesticide use for FY 1975-1979 is shown in Table 2. The data includes the use of dicamba for all purposes on USFS lands.

The BLM pesticide use report for FY 1979 for the State of Oregon indicates 0.5 lb/acre of dicamba (combined with one lb of 2,4-D/acre) was applied to 51 acres over 21 miles on weeds and grasses for road maintenance. 564 lbs of 2,4-D + dicamba was used on 937 acres for grass and brush in site preparation (10).

Dicamba is an effective plant growth regulator which alters root and shoot development and elicits a number of morphological responses including leaf malformation, increased branching, petiole and stem curvature, and abnormal flowering (11,12,13). It has been shown to destroy the phloem, cambium and associated parenchyma cells in nodal tissues of alligatorweed (14) and to inhibit mitosis in barley (15).

Dicamba is usually formulated as a highly water-soluble sodium, potassium or dimethylamine salt (16). It is frequently combined with other herbicides, particularly with phenoxy herbicides, to give wider spectrum weed control (17,18). Dicamba is registered for forest use as an oil-soluble liquid, a water-soluble liquid, and an emulsifiable concentrate (19). The dimethylamine salt in water and the oil-soluble formulation contain 4 lbs acid equivalent/gal (2). The dimethylamine salt can be applied in all seasons and is used undiluted or diluted 1:4 in water for cut surface injection into hardwoods or conifers (7,19). The dimethylamine salt plus 2,4-D is commonly applied in the spring to mid-summer to the foliage of shrubs and weed trees in site preparation (7,19). The oil-soluble acid of dicamba plus the isooctyl ester of 2,4-D is applied in the fall to late winter for shrub and weed tree control in site preparation (7,19).

The basic producer of dicamba in the U.S. is Velsicol Chemical Corporation which manufactures dicamba under a variety of trade names. Velsicol also produces dicamba in combination with other herbicides. For example, Banvel K and Weedmaster contain dicamba and 2,4-D. MonDak contains dicamba

TABLE 2. DICAMBA USE ON USFS LANDS IN REGION 6 FOR FY 1975-1979 (10)

FY	Herbicide	Pounds Used	Units Treated	Target Pest/Purpose
1975	dicamba	9	40 acres	For noxious and poison weed control/range management on NF* land
	dicamba	28	35 mi.	Road right-of-way
	Banvel 720‡	118.5	116.1 acres	On brush under powerlines on FS† land
	Banvel 520‡	unknown	2.5 acres	On brush under powerlines
	Banvel+2,4-D	300	161.2	On brush under powerlines
1976	dicamba	93	23 acres	For site preparation on FS land
	dicamba	640	298.5 acres	For right-of-way on FS land
	dicamba+2,4,5-T	--	27 acres	For right-of-way on FS land
	Banvel 120	7.5	--	For right-of-way on FS land
	Banvel 4 WS	176	--	For right-of-way on FS land
	Banvel 720‡	1.5	--	For right-of-way on FS land
1977	dicamba	25	50 acres	For noxious weed control on FS land
	dicamba+2,4-D	22 (dicamba)	8 si.mi.	Road right-of-way
	Banvel 720‡	3 (dicamba)	3 acres	For powerline right-of-way on FS land
	Banvel 4S	532	283 acres	For powerline right-of-way on FS land
1978	dicamba	27	110 acres	For noxious weed control on FS land
1979	dicamba	180	20 acres	For site preparation on National Forest System lands
	dicamba	15	29 acres	For noxious weed control

*NF = National Forest

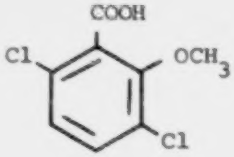
†FS = Forest Service

‡dicamba+2,4-D

and MCPA (4-chloro-2-methyl phenoxyacetic acid) (2). The major formulations of dicamba are listed in Table 3.

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF THE ACTIVE INGREDIENT

The active ingredient of dicamba is 3,6-dichloro-o-anisic acid (or 2-methoxy-3,6-dichlorobenzoic acid):



It is a white, crystalline solid with a melting point of 114°-116°C. It is poorly soluble in water but highly soluble in most organic solvents (16). The solubility at 25°C is as follows (3):

Solvent	Solubility, g/100 ml
Ethanol	92.2
Heavy aromatic naphthanes	5.2
Water	0.45
Xylene	7.8

The alkali metal and amine salts of dicamba are highly water soluble (16). The dimethylamine salt has a water solubility of greater than 72 g/100 ml.

Dicamba is stable to oxidation and hydrolysis and resistant to acid and strong alkali (3). Its vapor pressure is 3.41×10^{-5} mm Hg at 25°C (3) and 3.75×10^{-3} mm Hg at 100 °C (1).

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM IN PLANTS

Dicamba is rapidly absorbed by the roots or foliar tissues of plants and is readily translocated (21). The rate of absorption, movement and distribution in the plant may vary with the species (22,23) and with the stage of growth (12,24). Studies on a variety of plant species (grape, johnsongrass, bean, purple nutsedge, Tartary buckwheat, wheat, barley, wild mustard, Canadian thistle) have shown that root-absorbed dicamba is translocated to foliar tissues (1). Foliar-absorbed dicamba is translocated both basipetally

TABLE 3. VELSICOL'S BANVEL FORMULATIONS* (20)

Product	Concentration of Active Ingredient	Federally Registered Uses
Banvel Herbicide (water soluble liquid)	4 lbs/gal dicamba (DMA salt)	Field corn, Small grains, Sorghum, Pastures and Rangeland, Noncropland, Grass grown for seed, Tree injection, Harvest aid-Sorghum, Cropland rotated to wheat
Banvel 4S (water soluble liquid)	4 lbs/gal dicamba (DMA salt)	Lawns and Turf
Banvel + 2,4-D (water soluble liquid)	1.5 lbs/gal dicamba + 3 lbs/gal 2,4-D (DMA salt)	Lawns and Turf
Banvel K (water soluble liquid)	1.25 lbs/gal dicamba + 2.5 lbs/gal 2,4-D (DMA salt)	Field corn, Fall seeded wheat
Banvel 5G (granules)	5% dicamba (free acid)	Pasture, Rangeland, Noncropland
Banvel 4 O.S. (oil soluble liquid)	4 lbs/gal dicamba (free acid)	Industrial (tank mix with 2,4-D or 2,4,5-T only)
Banvel 4 W.S. (water soluble liquid)	4 lbs/gal dicamba (DMA salt)	Industrial (alone or tank mix with 2,4-D or 2,4,5-T)
Banvel 520 (oil soluble liquid)	1 lb/gal dicamba (free acid) 2 lbs/gal 2,4-D (isooctyl ester)	Industrial
Banvel 10G Granules	10% dicamba (free acid)	Brush
Banvel 2% Granules	2% dicamba	Lawns and Turf
MonDak (water soluble liquid)	1.25 lbs/gal dicamba 2.5 lbs/gal MCPA (DMA salts)	Wheat, Noncropland
Provel	0.23 lbs/gal dicamba 0.92 lbs/gal 2,4-D (DMA salts)	Lawns and Turf
Weedmaster (water soluble liquid)	1 lb/gal dicamba 3 lbs/gal 2,4-D (DMA salts)	Pasture and Rangeland, Noncropland
Banvel 720 (water soluble liquid)	1 lb/gal dicamba 2 lbs/gal 2,4-D (DMA salts)	Industrial
Banvel X.P. (pellets)	10% dicamba (free acid)	Pasture, Rangeland Noncropland
Brush Buster (water soluble liquid)	1 lb/gal dicamba 2 lbs/gal 2,4-D (DMA salts)	Brush and weed control, Noncropland

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*2,4,5-T formulations are excluded from this list. Many federally approved tank-mixes and combinations are available also.

and acropetally. It is continually redistributed from mature leaves to younger leaves and meristematic tissues. There is a limited amount of basipetal translocation to the roots and excretion into the surrounding soil or nutrient solution (1).

Dicamba metabolism in plants is species dependent (1,25). In wheat, bluegrass, Tartary buckwheat, wild mustard, barley and corn, the major pathway of dicamba metabolism appears to involve an initial ring hydroxylation at the 5 position followed by rapid formation of polar, acid-labile conjugates (1). In wheat and Tartary buckwheat, the majority of the 5-hydroxy-dicamba is probably conjugated as an O-glucoside (26,27). There are also minor pathways for dicamba metabolism in plants including demethoxylation to yield DCSA (3,6-dichlorosalicyclic acid) and DCGA (3,6-dichlorogentisic acid) which are also conjugated (1). Foy and Penner (30) found that dicamba inhibited the tricarboxylic acid cycle substrate oxidation by mitochondrial fractions isolated from etiolated cucumber cotyledons.

The metabolism of dicamba to 5-hydroxy-dicamba and its subsequent conjugation appears to be an effective detoxification mechanism in higher plants (1). Other ways in which residues can be dissipated are by exudation through the roots or by loss from leaf surfaces (28).

The persistence of dicamba in range forage grasses has been studied by Morton, et al. (29). Dicamba (DMA salt) labelled in the carboxyl position was applied at a rate of 1 lb/acre to pasture consisting of various range grasses over a three-year period. The amine salt of dicamba had an apparent half-life of two weeks in green tissues of silver beardgrass, little bluestem and dallisgrass. The average half-life of dicamba in the litter tissues was 2.6 weeks.

3.2 FATE IN SOIL

Processes which may affect the fate of dicamba in soil are volatilization, leaching and adsorption, runoff, photodecomposition, and degradation. Degradation appears to be primarily microbial.

3.2.1 Volatilization

Dicamba has been shown to volatilize from soil and leaf surfaces, but the extent and significance of losses due to volatility have not been determined (1). Gentner (31) showed that vapors from the soil-incorporated dimethylamine salt of dicamba were phytotoxic to beans. Burnside and Lavy (32), in studies using ^{14}C-carboxyl labelled dicamba (acid), showed that very little dicamba was lost over an 8-week period when dicamba-treated soils autoclaved prior to treatment were incubated at 35°C under various relative humidities (0-100 percent). On bare planchets, there was a loss of 48 percent at 35°C over a period of 11 weeks.

In recent studies by Behrens and Lueschen (33), dicamba volatility was examined in the field and in growth chambers. In the field experiments, potted soybeans exposed to vapors arising from corn foliarly-treated with various salts of dicamba developed dicamba injury symptoms. Dicamba volatilization was detected for three days after the application. In the growth chamber studies, the effects of dicamba volatility on soybeans were reduced by lowering the temperature or by increasing the relative humidity. Volatilization was influenced by the surface on which dicamba was deposited. The acid form was the most volatile and inorganic salts were the least volatile in growth chambers. However, in the field, the use of less volatile formulations did not eliminate symptoms on soybeans. The volatile component of the dimethylamine salt of dicamba was identified as free dicamba acid.

3.2.2 Adsorption and Leaching

Dicamba is considered to be a very mobile pesticide (34,35,36). In studies using soil thin layer chromatography to evaluate the mobility of 40 pesticides on Hagerstown sicl soil (2.5 percent organic matter, 39.5 percent clay, pH 6.8), Helling (34) found that dicamba was one of the most mobile pesticides tested with an R_f value of 0.96. R_f values for the pesticides tested ranged from 0 to 0.96. In further studies on 14 surface soils with 13 pesticides, Helling (35) found that dicamba was the most mobile pesticide tested. Dicamba mobility was significantly correlated with pH at the 5 percent level with greater mobility occurring at higher pH.

Other studies on the relative mobility of 28 herbicides in silty clay loam and sandy loam soils using soil columns have shown that dicamba was second only to 2,3,6-trichlorobenzoic acid (2,3,6-TBA) in mobility (37).

Grover (38) studied the movement of dicamba in five Canadian prairie soils using soil columns. The relative movement of dicamba indicated an inverse relationship between adsorption and mobility in soil. The volume of water required to leach 50 percent of the dicamba through the soil columns varied from 13 ml to 35 ml with larger volumes required for soils with greater amounts of organic matter.

The ready movement of dicamba in soil suggests that there is a limited amount of adsorption to soil particles or colloids (39). In general, adsorption studies have shown that dicamba is adsorbed onto kaolinite clay but that there is little adsorption onto other clays and soil types studied (32). It was suggested that the adsorption onto kaolinite was due to its considerable anion adsorption capacity. (Electrophoresis studies have shown that dicamba behaves as an anion over the pH range 4.1 to 9.4.) Carringer, et al. (41) studied adsorption and desorption of dicamba on soil organic matter and Ca-saturated montmorillonite. Dicamba was adsorbed by the montmorillonite but not by organic matter. Only 9.54 percent of the applied dicamba was desorbed using deionized water while 41.6 percent was desorbed with 1 N $CaCl_2$. This suggests that some dicamba was strongly adsorbed. In studies on adsorption of dicamba by humic acid, Khan (42) found that humic acid could retain dicamba in amounts of 44 μ moles dicamba per 1 g of humic acid. Prolonged washing with distilled water did not release any herbicide. It was concluded that this complexing of dicamba and humic acid could affect the activity, behavior, bioavailability and survival rate of dicamba in the soil and aquatic environment. Other studies on adsorption of the major degradation product of dicamba, 3,6-DCSA, indicate that at least 30 percent is adsorbed to all soil types (40). The greatest adsorption of DCSA occurred on silty clay soil (55 percent) while the least amount was adsorbed to the sandy loam soil (30 percent).

Dicamba is readily leached from soils (43,44). Studies in soil columns show that the dimethylamine salt of dicamba followed slightly behind the forward penetration of added water in both loam and sandy loam soils (39). In studies with dicamba (acid) applied to 1.5 x 1.5 m plots of silt loam soil in a humid, temperate climate at rates of 1.1, 2.2, and 4.5 kg/ha, small amounts of dicamba leached to a depth of 10-20 cm (45). None was detected below 20 cm. However, results obtained with the acid may not be representative of the more commonly used dimethylamine salt form which is expected to move readily through the soil when excessive rainfall occurs (32). In another study, Banvel D was applied to a lysimeter with silt loam soil at a rate of 5.6 kg active ingredient/ha (46). Residues of dicamba at 0.7 ppb were first detected in the percolation water 10 months after application. Subirrigation and surface evaporation studies by Harris (44) have shown that dicamba may also move upward in the soil profile, depending on the water flux and capillary water movement.

3.2.3 Runoff

The salts of dicamba are highly water-soluble and readily enter the soil. Therefore, contamination of local surface waters due to runoff is unlikely except in the event of heavy rainfall very shortly after dicamba application. The loss of dicamba in runoff water was determined on sod and fallow clay loam soil plots with slopes of 3 percent and 8 percent (47). The dimethylamine salt was applied at a rate of 1-2 lb/acre and simulated rainfall of 0.5 in/hr was applied 24 hours after dicamba application. Of the 177 L of water applied, 15 L were recovered as runoff. The concentration of dicamba in the runoff and the total amount of dicamba from sod and fallow plots with a 3 percent slope are as shown:

Soil Cover	Dicamba Concentration, μg/ml Time After Application 24 hr.	 4 mo.	Total Dicamba (lb/A) Time After Application 24 hr.	 4 mo.
Sod	4.81	0	0.065	0
Fallow	1.60	0.018	0.017	0.0032

Bean plant bioassays indicated that there was sufficient dicamba in 100 ml of runoff water obtained 24 hours after application to kill the plants. Four months after application, the amount was not sufficient to kill the plants.

In another experiment, Banvel D was applied in May to a lysimeter and to an adjacent soil plot (4.1 m^2) of silt loam soil at a rate of 5.6 kg active ingredient/ha, a rate 3-10 times the rate commonly used for weed control (46). Runoff samples collected after storms in August and September contained 0.23 and 0.54 ppm, respectively.

Norris and Montgomery (48) analyzed stream water samples for dicamba following forest application of 1.12 kg dicamba per ha in 37.8 liters of water. Samples of water were collected periodically for nearly 14 months after application, but no dicamba residues were found more than 11 days after application despite the persistence and leaching characteristics of dicamba and the potential for runoff.

3.2.4 Photodecomposition

Photodecomposition is probably not a major route for dicamba degradation. Bioassays for aqueous dicamba solutions (0.0625 to 1 ppmw) exposed to sunlight for up to 16 days indicate that dicamba toxicity remained at a level sufficient to inhibit growth of cucumber roots (49). Although there was a slight decrease in toxicity, it could have been due to biological degradation.

3.2.5 Degradation

The degradation of dicamba is favored in soils high in organic and moisture content, and at higher temperatures. Research suggests that dicamba degradation is, to a large extent, due to microbial breakdown. Burnside and Lavy (32) applied ^{14}C-labelled dicamba to silty clay loam, silt loam, and sandy loam soils and incubated them at moisture levels 13 percent and 18 percent of field capacity at temperatures of 15°, 25°, and 35°C. Soybean bioassays were used to test the phytotoxicity of dicamba over a 9 month period. Detoxication was found to be greater in soils with more organic matter, in soils with a higher level of moisture, and at higher temperatures. In greenhouse studies using five soils, the amount of dicamba initially required to reduce the fresh weights of snap beans was found to increase as the clay and organic matter increased (50). Hahn, et al. (49) using cucumber bioassays, found that dicamba was degraded faster in silty clay loam soil than in sandy loam soil, faster in surface soil than in subsurface soil, and faster at higher temperatures. It was suggested that degradation is likely to occur faster in those soils with the relatively high organic matter levels (e.g., the silty clay loam and the top-soil) because of larger microbial populations.

In laboratory studies on three prairie soils, high organic silty clay, sandy loam, and heavy clay, Smith (51) found that dicamba disappearance was most rapid on the silty clay soil. Breakdown of dicamba took 2 weeks at all moisture levels. In the sandy loam and heavy clay soils, however, degradation was dependent on the soil moisture. At a high moisture level (35 percent), less than 10 percent of the applied dicamba was detected after 4 weeks. At levels near the wilting point, residues were still detected after 6 weeks. When the three soils were sterilized prior to dicamba application, over 90 percent of the dicamba was recovered after 4 weeks.

Smith (40) also studied degradation of ^{14}C-ring and ^{14}C-carboxyl labelled dicamba in moist, non-sterile, heavy clay in flasks at 25°C. Over 50 percent of the dicamba was lost within 4 weeks. The sole degradation products were 3,6-dichlorosalicyclic acid (3,6-DCSA) and CO_2. In additional studies, Smith (40) compared the decomposition of ^{14}C-ring labelled dicamba in 3 soils: silty clay, heavy clay, and sandy loam. There was a buildup of 3,6-DCSA as dicamba degraded, followed by a slow loss of DCSA which was complete in 9 weeks. In steam sterilized soils, there was negligible breakdown of dicamba.

Burnside, et al. (53) followed the dissipation and detoxification of dicamba for 6 years at three locations in Nebraska. The soil types and characteristics were as follows:

Soil Type	% Sand (2-0.05 mm)	% Silt (0.05-0.002 mm)	% Clay (0.002 mm)	pH	Moisture % at 15 atm	Organic Matter, %	C.E.C. meq/100g
Rosebud loam	49	32	19	6.8	8.6	1.2	15
Holdrege loam	37	41	22	7.1	10.8	2.6	20
Sharpsburg silty clay loam	2	59	39	5.8	14.3	4.4	24

Dicamba was applied at 5, 10, and 20 lb/acre and its persistence was determined by field bioassays growing field beans and soybeans. Field bean yields were significantly reduced only in rosebud loam sprayed with 20 lb/acre dicamba (an average 40 percent reduction in yield). Dicamba apparently did not persist at other application rates or in the other soils.

Smith and Cullimore (52) studied the effects of temperature variation on the microbial degradation of ^{14}C-carboxyl labelled dicamba applied at 2 ppm to three prairie soils (sandy loam, silty clay, and heavy clay) at field capacity moisture levels. No loss of dicamba was observed in any soil at -5°C. In silty clay soil, more than 80 percent of the dicamba was degraded at temperatures above 15°C after 8 days. In sandy loam and heavy clay soils, over 80 percent of the dicamba was degraded between 20° and 35°C after 14 days.

Studies have shown that the pH of the soil also influences the degradation and/or phytotoxicity of dicamba. Corbin and Upchurch (54), using high organic matter soils, determined that the optimum pH for detoxification of dicamba is 5.3. Cucumber seed assays showed complete detoxication of 14.4 ppm within 4 weeks. At pH 7.5, dicamba persisted. Another study indicated that the phytotoxicity of dicamba increases as the soil pH increases, reaching a maximum at pH 6.5 and 7.5 (55). The reported persistence of toxic concentrations of dicamba has varied from 30 days (32) to over one year (57). However, based on the studies reviewed below, under field conditions, dicamba will probably not persist more than several months in most soils. This is likely to be the case for forest soils which usually have high levels of organic matter and moisture. Smith (51) applied 1.1 kg/ha of dicamba to field plots 20 x 20 cm and analyzed the soil for dicamba residues approximately six months after application. No residues were recovered at depths up to 15 cm in soil. Altom and Stritzke (56) applied the dimethylamine salt of dicamba in a water solution to forest and grassland soils to give a concentration of 2.47 ppm (W/W). Soil samples were taken over a period of 100 days. The half-life of dicamba ranged from 17 to 32 days in the soils tested. In other studies, an amine salt of dicamba was applied to the surface of a silty loam soil (1.5 x 1.5 m plots) in a humid, temperate climate at the rates 1.1, 2.2, and 4.5 kg acid equivalent/ha (45). After 42 days, about 5 percent of the applied dicamba remained.

Dicamba was applied to Texas grassland soils with neutral to slightly basic pH and low organic matter content at application rates of 0.28, 0.56, 0.84, and 1.12 kg/ha (58). Data indicated that 1.12 kg/ha or less of applied dicamba will dissipate during the growing season following spring application. Residues were not found below 180 cm at any time in any soil up to 53 weeks after application at the rates used.

3.3 PERSISTENCE IN WATER

Few studies have been conducted on the persistence and degradation of dicamba in water. In one field study, 1.12 kg/ha of dicamba and 2.24 kg/ha of 2,4-D in 37.8 l water was aerially applied to 67 ha of a 244 ha forestland watershed (48). Residues were found at the first sampling point about two hours after application. Residue levels rose to a maximum of 37 ppb in about 5.2 hours and then slowly declined to background levels by 37.5 hours. No dicamba residues were found more than 11 days after application. The authors concluded that dicamba could have been adsorbed by stream sediments or taken up by aquatic biota.

The fate of dicamba in water has also been studied using a model ecosystem containing sand, water, and a series of food chain organisms compatible with conditions in the aquarium (59). Using this model ecosystem, ^{14}C-carboxyl labelled dicamba in acetone was applied to the leaves of sorghum plants (60). The concentration of dicamba and its metabolites in the water reached a peak the 6th day after application and then slowly decreased, indicating that decarboxylation of dicamba does not occur rapidly. About 0.2 percent of the radioactive materials could be ether-extracted from raw water. After hydrolysis with HCl, 98.8 percent could be extracted. It was concluded that most of the dicamba and its metabolites persisted in conjugated or in anionic forms in water. After hydrolysis, dicamba was slowly transformed to 5-hydroxydicamba (about 10 percent after 32 days).

4.0 IMPACTS ON NON-TARGET ORGANISMS

4.1 PHYTOTOXICITY

The sensitivity of plants to dicamba varies considerably (61). Dicamba selectivity depends on differences in its distribution within a plant species and differences in the rate of absorption, translocation, and metabolism (1). Rapid metabolism in tolerant plants detoxifies dicamba (26), effectively reducing the concentration of highly mobile unchanged dicamba which is available for transport to sensitive target sites (1).

Dicamba has been found to be phytotoxic to many deciduous shrubs and trees, conifers, and forbs (7). Patric and Campbell (62) have categorized plants in West Virginia according to their susceptibility to dicamba. These categories are shown in Table 4. These examples illustrate the broad spectrum of plant species affected by dicamba.

4.2 TOXICITY TO FISH, BIRDS, WILDLIFE, AND INSECTS

Dicamba has a low order of acute toxicity for oral, dermal and inhalation exposure to mammals (28). Table 5 gives some toxicity values for

TABLE 4. SENSITIVITY OF PLANTS IN WEST VIRGINIA TO DICAMBA (62)

Least Susceptible

American beech
Fern
Hickory
Striped maple
White ash
Chestnut oak
Grasses
Sedge
Sugar maple
Witch hazel

Intermediate in Susceptibility

Blackberry
Black cherry
Chestnut
Deertongue grass
Fireweed
Loosestrife
Red oak
Serviceberry
Violet
Black birch
Black gum
Cucumber tree
Dock
Flowering dogwood
Red maple
Sassafras
Sourwood

Most Susceptible

American elder
Bindweed
Blueberry
Mulkin
Pin cherry
Puckley ash
Smartweed
Teaberry
Azalea
Black locust
May apple
Nettle
Pokeweed
Sheep sorrel
Staghorn sumac
Twisted stalk

specific formulations. Dicamba is not a skin irritant although some formulations are extremely irritating and corrosive to the eyes (28). When fed to rats as the DMA salt over a period of about 13 weeks, Banvel produced an overall no-effect level at 500 ppm. As indicated in Table 5, dicamba also has a low level of toxicity to wildfowl. Dicamba is more toxic to fish than to birds or mammals.

Dicamba has been shown to be relatively non-toxic to bees. When fed to honeybees in a 60 percent sucrose solution at concentrations of 0, 10, 100, and 1000 ppmw, dicamba and the dimethylamine salt of dicamba did not cause any significant differences in the half-life of bees at any concentration

TABLE 5. TOXICITY OF SOME FORMULATIONS OF DICAMBA TO SELECTED SPECIES

Formulation	Species	Test	Results	Reference
Technical Banvel	Rat	Oral LD_{50}	1707-2900 mg/kg	28
Banvel, 4 lbs/gal DMA	Rat	Oral LD_{50}	1028-2629 mg/kg	28
Dicamba DMA salt	Rat	Oral LD_{50}	2900 mg/kg	65
Technical Banvel	Rabbit	Dermal LD_{50}	>2000 mg/kg	28
Banvel, 4 lbs/gal DMA	Rabbit	Dermal LD_{50}	>2000 mg/kg	28
Technical Banvel DMA	Rat	Inhalation LC_{50}; 4-hour exposure	>200 mg/l	28
Banvel - 310, 4 lbs/gal DMA	Rat	Inhalation LC_{50}; h-hour exposure	>200 mg/l	28
Technical Banvel (86.8% A.I.)	Mallard duck	Acute oral LC_{50}	2000 mg/kg	28
Technical Banvel (86.8% A.I.)	Mallard duck, Bobwhite quail	8-day dietary LC_{50}	>10,000 ppm >10,000 ppm	28
Banvel, XP (10% A.I.)	Mallard duck, Bobwhite quail	8-day dietary LC_{50}	>10,000 ppm >10,000 ppm	64
Banvel - 310, 4 lbs/gal DMA	Mallard duck, Bobwhite quail	8-day dietary LC_{50}	>4640 ppm	28
Technical, Banvel - 310	Mallard duck	Acute oral LC_{50}	2000 mg/kg	64
Technical Banvel	Bluegill sunfish,	96-hour LC_{50}	135 mg/L	28
	Rainbow trout,	96-hour LC_{50}	135 mg/L	28
	Daphnia	48-hour LC_{50}	111 mg/L	28
Banvel, 4 lbs/gal DMA	Bluegill sunfish	96-hour LC_{50}	>1000 mg/L	28
Dicamba DMA salt	Bluegill sunfish,	48-hour LC_{50}	130 ppm	63
	Rainbow trout	48-hour LC_{50}	35 ppm	63
Technical Banvel (86.8% A.I.)	Sheephead minnow	96-hour LC_{50}	>180 mg/L	28,64
Same	Grass shrimp	96-hour LC_{50}	>100 mg/L	28,64
Same	Fiddler crab	96-hour LC_{50}	>180 mg/L	28,64

(66). When bees were dusted with dicamba at a dose of 91 μg/bee, mortality was 2.6 percent (67). For comparison with field conditions, an application rate of 1 kg/ha would give a dose of 1.12 μg/bee. Therefore, at recommended application rates, dicamba is considered relatively non-toxic to bees.

4.3 BIOACCUMULATION

Dicamba does not tend to bioaccumulate in animals. In rats, it is rapidly excreted in the urine with approximately 20 percent of the urinary metabolites in the form of glucuronic acid conjugates (69). Because of its high solubility, most dicamba residues are in the aqueous parts of the body rather than in fatty tissues (68). Studies using a model ecosystem have provided no evidence that dicamba or its metabolites are magnified in the food chain (60). The total equivalent of radioactivity decreased from 1.6 ppm in algae to 0.02 ppm in fish in the model ecosystem food chain involving algae to mosquito to fish (60).

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Common Name: 2,4-D

Chemical Name: 2,4-dichlorophenoxyacetic acid

Major Trade Names: Weedone LV-4; Esteron 99 Concentrate; Weedar 64; Verton 2-D

Major Applications in Forestry: Used in the Pacific Northwest and Great Lakes primarily as a selective broadleaf weedkiller in connection with site preparation. Has limited use for release.

SUMMARY

Most of the available data on the fate of 2,4-D in soil and water is the result of laboratory or field studies in non-forest systems. There is limited data available in connection with applications to forests.

Plants readily absorb, translocate and metabolize 2,4-D. The formulation influences the degree of absorption. Once absorbed, 2,4-D may be chemically altered by a variety of mechanisms. Since brush usually resprouts within a year after spraying 2,4-D on forest lands, it is believed that residues at phytotoxic levels do not persist in the vegetation.

2,4-D is considered to be a relatively nonpersistent herbicide. The most persistent form of 2,4-D in the environment is the acid. Esters and amines of 2,4-D hydrolyze to the acid within a few days in the soil. Degradation of the acid is primarily microbial. In warm, moist soils with a high organic content, 2,4-D can degrade within days, but 2,4-D can persist for many months in the absence of favorable soil conditions. Leaching of 2,4-D is more extensive in soils with lesser amounts of organic matter and with a lower pH. Leaching and adsorption are inversely related. In general, 2,4-D remains within the top foot of the soil surface.

In water, esters of 2,4-D are rapidly hydrolyzed to the acid form. The persistence of the acid depends on the presence of microorganisms adapted to 2,4-D degradation. In cool, nutrient-poor, natural surface waters, 2,4-D may remain stable for many months. Photodecomposition has been demonstrated in the laboratory although the degree of 2,4-D degradation in the field with natural sunlight is unknown. Volatilization is usually not a major mechanism for removal of 2,4-D from water.

2,4-D is phytotoxic to numerous non-target plant species including some crops and ornamentals. Conifers are susceptible during periods of rapid growth. The toxicity of 2,4-D to fish is highly variable depending on the species, the water quality, and the 2,4-D formulation. The acute oral LD_{50} of 2,4-D for some birds ranges from 300 to 5000 mg/kg. It is generally less toxic to birds than to mammals. The toxicity of 2,4-D to honey bees is low. 2,4-D does not tend to bioaccumulate in fish or in mammals.

1.0 INTRODUCTION

The compound 2,4-dichlorophenoxyacetic acid (2,4-D) is a phenoxy herbicide related to the herbicides 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 4-chloro-2-methyl phenoxyacetic acid (MCPA). It was introduced as a selective weedkiller at the end of World War II following the discovery of its activity as a plant growth regulator (1). The value of 2,4-D lies in its effectiveness as an herbicide against dicotyledonous, but not monocotyledonous plants. Consequently, it has been used to selectively kill broadleaf weeds in cereal grains, pastures, grasslands, and forests.

Forest uses of 2,4-D have been primarily in connection with site preparation. Because of possible injury to conifers, 2,4-D has limited application for "release" in coniferous forests.

2,4-D is an active analog of the plant growth hormone, indole-2-acetic acid (IAA) (1). IAA is an auxin, an organic substance which promotes growth along the longitudinal axis of shoots and inhibits elongation of roots. 2,4-D can take the place of IAA in reactions controlling plant growth, thus causing loss of normal growth control. The uptake and translocation of 2,4-D from the surface of the plant will result in increased auxin concentrations in many plant tissues, including those that normally have low concentrations. Normal growth is disrupted as some tissues are stimulated to regrowth and others are inhibited in their development.

In addition to affecting the activity of enzymes, 2,4-D also affects cell division and differentiation and synthesis of nucleic acids and proteins (1).

Formulations of 2,4-D recommended for use in forestry and ranges include (2):

a) Low volatile esters (propylene glycol butyl ether ester, butoxyethanol ester, isooctyl ester);

b) High volatile esters (isopropyl ester, butyl, n-butyl, and isobutyl esters, ethyl ester);

c) Water soluble amines (dimethylamine, triethanol amine, triisopropyl amine);

d) Oil soluble amines (dodecyl amine, tetradecyl amine, n-oleyl-1, 3-propylene diamine);

e) The parent acid;

f) Inorganic salts (sodium, potassium, lithium, ammonium).

Water soluble and oil soluble amine salts account for a small proportion of the total use of 2,4-D for forestry and range purposes. Water soluble amines are generally used for cut surface or injection into individual stems. Oil soluble amines are used as foliage sprays in areas where use of low volatile esters may not be suitable due to potential for vapor drift and damage to non-target vegetation. Low volatile esters account for 80 to 90 percent of all forest improvement spray projects (2). They are commonly applied as foliage sprays (by hand gun or backpack mist blower). Aerial application or ground rig applicators are also used (2). Applications in forestry are at the rate of 2 to 4 lbs acid equivalent of active ingredient per acre. Once in the environment, all formulations of 2,4-D are degraded to the parent acid.

In the United States, there are four basic producers of 2,4-D: The Dow Chemical Co.; Fallek-Lankro Corp.; Rhone-Poulenc, Inc.; and Vertac Chemical Corp. (3). Some of the manufacturers as well as a number of other companies formulate and distribute the product. Trade names of some formulations of 2,4-D commonly used in forestry include (3,4):

- Rhodia 2,4-D Low Volatile Ester 46 (isooctyl ester of 2,4-D);
- Weedone 170 (butoxyethanol ester of 2,4-D and 2,4-DP);
- Weedone LV-4 (butoxyethanol ester of 2,4-D);
- Esteron 99 Concentrate (propylene glycol butyl ether ester of 2,4-D);
- Formula 40 (an amine of 2,4-D);
- Weedar 64;
- Verton 2-D;
- DMA-4 (dimethylamine salt of 2,4-D).

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF THE ACTIVE INGREDIENT

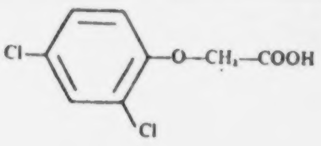
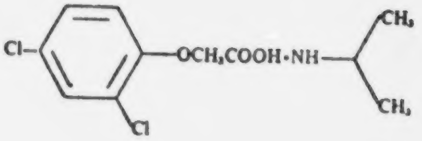
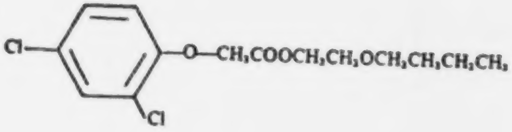
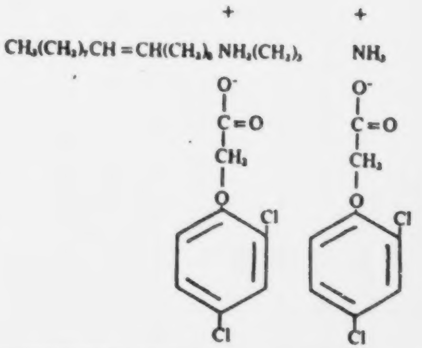
Solubility, vapor pressure and chemical structures for some important formulations of 2,4-D are presented in Table 1.

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM IN PLANTS

Studies on the uptake and metabolism of 2,4-D in plants have been re-

TABLE 1. CHEMICAL AND PHYSICAL PROPERTIES OF 2,4-D (5)

Formulation	Solubility	Vapor Pressure	Structure
2,4-D (acid)	0.09 g/100g, 25°C, water 85.0g/100g, 25°C, acetone*	0.4 mm Hg, 160°C	
2,4-D amine (dimethylamine salt of 2,4-D)	300g/100g, 20°C, water soluble in methyl, ethyl and isopropyl alcohols and acetone. Insoluble in kerosene, diesel oil.	--	
Low volatile 2,4-D ester (butoxyethanol ester)	Soluble in most organic solvents; insoluble in water.	4.5×10^{-6} mm Hg, 25°C^{957}	
Oil soluble amine salt (N-oleyl-1,3 propylene-diamine salt)	Insoluble in water; soluble in most organic solvents.	--	

*See the source reference for solubility in a number of other solvents.

viewed by Loos (1). 2,4-D is absorbed through leaves, stems, or roots and translocated throughout the plant. The formulation significantly influences adsorption. Formulations with a low lipid solubility (e.g., 2,4 -D salts) penetrate poorly, particularly in an application medium with a high pH (1). Esters are readily absorbed, although some may damage the translocation mechanism of the plant. However, esters formed from long chain alcohols with lipophilic and hydrophilic properties (e.g., butoxyethanol esters) are effectively absorbed and translocated (1).

Inclusion of surface active compounds as emulsifying agents in 2,4-D formulations often increases herbicidal activity, probably by increasing absorption; high humidity also increases uptake.

While 2,4-D is readily absorbed into the roots of plants, translocation is not as effective as with uptake by the leaves or stem (1). Once absorbed by plants, 2,4-D may undergo chemical alteration in one or more of the following ways (1):

a) Degradation of the side chain (observed in many species);
b) Side chain lengthening (a few cases);
c) Hydroxylation of the ring (a well-established metabolic reaction);
d) Conjugation with plant constituents (e.g., glucose ester of 2,4-D, 2,4-dichlorophenoxyacetyl-aspartic acid);
e) Ring cleavage (rare); and
f) Formation of various metabolites.

Norris and Freed (7) studied the metabolism of 2,4-D in bigleaf maple, a large deciduous woody plant commonly found in forest lands of the Western U.S. They found that decarboxylation in treated foliage was not an important detoxification mechanism. In another study, Norris (6) found that brush usually resprouts within a year following spraying on forest lands with 2,4-D. This suggests that high levels of phytotoxic residues of 2,4-D do not persist in vegetation.

Morton, et al. (8) sprayed 2,4-D labelled in the carboxyl position on pasture consisting of various range grasses over a three-year period. The acid of 2,4-D was applied at rates of 0.5 to 2 lb/acre while the DMA salt of 2,4-D was applied at the rate of 1 lb/acre. Samples were taken up to 16 weeks after treatment. The average half-life of 2,4-D in green and litter tissues was 2.3 and 2.8 weeks, respectively. Extracts of green tissue harvested one hour after treatment with the acid yielded only the acid of 2,4-D; tissue harvested one week after treatment contained both acid and unknown metabolites.

3.2 FATE IN SOIL

Processes which may affect the fate of 2,4-D in soil are photodecomposition, volatilization, leaching, adsorption, runoff and chemical and microbial degradation. However, the extent of photodecomposition of 2,4-D on the surface of forest soil has not been studied. In water, 2,4-D can undergo photodecomposition under uv radiation or sunlight but, regardless of whether this mechanism operates in soil, photodecomposition would not be expected to significantly contribute to the disappearance of 2,4-D from forest soil due to minimal exposure to sunlight.

3.2.1 Volatilization

Volatilization will depend on the vapor pressure of the 2,4-D formulation. The acid, salts, and amines are less volatile than the esters, with the oil soluble amines being the least volatile form (5). Volatility also occurs to a greater extent in soils with low organic matter and clay content (9). No studies making quantitative measurements of volatilization were located. One study, however, on the fate of the 2,4-D dimethylamine salt (DMA-2,4-D) and 2,4-D isooctyl ester in a fine silty loam soil suggested volatilization as a means for disappearance of 2,4-D from soil (10). One hour after 2,4-D was applied under field conditions, considerably more amine than ester was recovered from the soil. After 6 months, an average of 0.04 ppm of 2,4-D remained in the soil regardless of formulation, application rate, or cropping scheme. It was suggested that the lower initial recovery of the ester may be due to its volatilization; however, no measurements were taken to confirm this.

3.2.2 Adsorption and Leaching

The adsorption capacity of a given soil for 2,4-D affects the potential for leaching of 2,4-D from soil. The leaching tendency would be lower with those soil types and under those conditions which promote adsorption.

The extent to which 2,4-D is adsorbed in soil has been correlated with the organic matter content of the soil and the soil pH. Grover (11) studied the movement of 2,4-D in five Canadian soils using soil columns. The relative movement of 2,4-D in the soil indicated an inverse relationship between adsorption and mobility. The volume of water required to leach 50 percent of the 2,4-D through the soil columns varied from 16 to 140 ml. Larger volumes were required for soils with greater amounts of organic matter. There was also some correlation with pH; 2,4-D leached more readily in soils with a higher pH. No correlation was found between leaching and the clay content of the soil.

Other studies have shown that clay does not strongly adsorb 2,4-D. Frissel and Bolt (13) observed negative adsorption of 2,4-D on montmorillonite at low salt concentrations and at pH greater than 4.0 and on illite at pH greater than 7.0.

Aly and Faust (12) determined the sorption of the sodium salt, the isopropyl, butyl and isooctyl esters of 2,4-D and 2,4-dichlorophenol on 3 clay minerals: kaolinite, bentonite (a montmorillonitic clay) and illite. In general, the sorbed amounts were very small, ranging between 0.02 and 0.14 mg per gram of clay at an applied concentration of 5 mg per liter. Since natural waters have low salt concentrations and have pH values between 6.0 and 8.0, suspended clays in surface waters are not expected to carry significant amounts of 2,4-D.

The kinetics of adsorption and desorption of 2,4-D on forest soil material were studied by Norris (14) in laboratory tests. The following data on percent attainment of equilibrium for adsorption and desorption were reported as a function of time.

Time, min.	% Attainment of Equilibrium Adsorption	% Attainment of Equilibrium Desorption
5	44	--
10	62	67
15	65	--
20	56	74
30	74	82
60	82	89
120	79	95
180	94	97

The above data indicate a relatively rapid rate for both adsorption and desorption for the system studied.

Helling and Turner (15) evaluated pesticide movement by comparing R_f values on thin layers of soils (the R_f value is a quantitative indication of the front of pesticide movement and a reproducible index of mobility). Pesticides were categorized in classes 1 through 5, in order of increasing mobility. Based on these studies, 2,4-D is relatively mobile in soil - it is considered to be a class 4 pesticide.

Despite its potential mobility, 2,4-D usually remains within the top few inches of soil (16). The extent to which 2,4-D will leach into soil is determined by the formulation, the soil properties and the amount of water moving through the soil. Salts of 2,4-D, which are polar, are more readily leached in sandy soils than esters, which have a lower water solubility (9).

Other soil types have been tested with similar results. In these experiments, 2,4-D in water solutions was applied to tubes of silty clay loam top soil to determine the effect of flooding conditions on the leaching of herbicides (17). An alkanolamine salt of 2,4-D (with 100 percent solubility) leached 15 inches whereas the butoxyethanol ester (solubility of 16 ppm) leached only 3 inches.

The leaching of 2,4-D has been studied in field plots of silty loam soil to which simulated rainfall was applied one day after application of 2,4-D amine and ester to the soil (10). Two days later, 2,4-D was found to a depth of 24 cm. Five days after application, 2,4-D was found to a depth of 40 cm. It continued to move downward in the soil for 30 days after herbicide application.

3.2.3 Runoff

Studies on runoff from 2,4-D amine and 2,4-D ester-treated agricultural plots (1.5 m x 4.5 m) with a slope gradient of 16 to 17 percent showed that 2,4-D can be lost from fields within a few days after application if sufficient rainfall occurs (10). The extent of 2,4-D recovered in runoff increased with higher rates of herbicide application. The concentration of 2,4-D amine in the collected runoff was 4.5 ppm and 2.0 ppm for application rates of 11.2 kg/ha and 1.1 kg/ha, respectively. At these same application rates, the concentrations of 2,4-D ester in the runoff were 3.4 and 2.0 ppm, respectively.

Since the esters of 2,4-D do not leach into the soil as readily as water soluble formulations, they may have a greater potential for runoff from soil. At least one study suggests that this is the case. As much as 27 percent of the 2,4-D ester washed from the soil surface of a sandy loam soil in a test plot in which artificial rain was applied (18). Under similar conditions, using the more water soluble 2,4-D amine, only 3 percent of the 2,4-D was lost.

3.2.4 Chemical and Microbial Degradation

Degradation of 2,4-D in the soil is to a large degree dependent on the soil conditions such as organic content, moisture and temperature. Under favorable conditions (i.e., high organic content, adequate moisture and warm temperatures), 2,4-D is not expected to persist in soil for an appreciable length of time. Under such favorable conditions, a half-life of 4 to 5 days has been reported (19).

Only limited data on the persistence of 2,4-D in forest soils or under conditions simulating those in various forests are available. Norris (20) reports that 2,4-D was readily degraded in forest floor material collected beneath red alder. Thirty-five days after application of 2.24 kg/ha of 2,4-D (2 lb/acre), only 6 percent was recovered in the floor material. Recovery was similar for 2,4-D applied at 4.48 kg/ha.

Breakdown of 2,4-D in the soil depends on the soil temperature, moisture, the organic matter content of the soil and the soil aeration. In the late 1940's, researchers provided evidence for microbial degradation when they demonstrated that 2,4-D degradation was stimulated by warm, moist conditions and the addition of organic matter to the soil. Degradation was inhibited in air-dried and autoclaved soils. According to Loos (1), Audus was the first to conclusively demonstrate (in the early 1950's) the role of microorganisms in the degradation of 2,4-D in soil.

Field studies on the degradation of 2,4-D acid have been recently conducted in Nebraska using silty clay loam and sandy loam soils (21). Soils were tested at depths of 0-23 cm, 36-61 cm, and 90-122 cm. All of the 2,4-D was degraded at all depths (15-, 40-, and 90-cm) during the first 5 months under aerobic conditions. Under anaerobic conditions, the rate of degradation in silty clay loam was similar to the rate under aerobic conditions, whereas in sandy loam soil under anaerobic conditions, a significant amount of 2,4-D remained at all 3 depths. Since soils higher in organic content (in this case, the silty clay loam) can support a larger microbial population, they have a better chance of containing the facultative microorganisms required to degrade 2,4-D under both aerobic and anaerobic conditions.

The potential for soil organisms to degrade 2,4-D depends on possession of the enzyme system required to metabolize compounds structurally similar to 2,4-D. Consequently, a soil that has had sufficient prior exposure to 2,4-D and has developed an appropriate microbial community may be able to degrade 2,4-D at a faster rate. Pathways for the degradation of 2,4-D have been demonstrated in *Arthrobacter* and in *Pseudomonas* (1). The most important mechanism involves removal of the acetic acid side chain to yield 2,4-dichlorophenol. This is followed by ring cleavage and finally degradation to produce aliphatic acids (e.g., succinic acid). In the soil, ester and amide forms of 2,4-D are first converted to the parent acid form prior to degradation. The conversion to the acid form may be brought about through enzymatic hydrolysis by microorganisms (22).

Isooctyl esters of 2,4-D and mixed amines of 2,4-D were applied to the surface of a silty loam soil in a humid, temperate climate to determine soil persistence (23). The following application rates were used:

Active Ingredient	Rate, kg/ha AE
Isooctyl esters of 2,4-D and 2,4,5-T	7.8* 15.7* 31.4*
Mixed amines of 2,4-D	5.6 11.2 22.4

---

*Rate of each ingredient

None of the 2,4-D isooctyl esters was detectable in the soil after 14 days. The major residue in soil after application of the ester was the free phenoxy acid which reached a maximum concentration in the 14-day soil samples. After 70 days, 1 percent of the applied 2,4-D remained in the soil from the plots treated with 7.8 kg/ha and 31.4 kg/ha; 2 percent remained on the plots treated with 15.7 kg/ha. No 2,4-D was detected past 55 weeks.

In plots treated with the amine of 2,4-D, maximum soil residues (free phenoxy acid) occurred after 14 days. Less than 5 percent of the 2,4-D remained at the end of 70 days. Some 2,4-D penetrated 10-20 cm into the soil but none was detected below that level.

As noted previously, conversion of esters and amines of 2,4-D to the parent acid may be brought about by microbial degradation. However, there is evidence that chemical hydrolysis may be responsible for this conversion in some cases.

In studies on hydrolysis of 2,4-D esters to 2,4-D in Saskatchewan soils, the following results were obtained in samples analyzed after 24 hours (24):

Soil Type	Moisture Content	Ester Recovered		
		n-butyl	Isopropyl	Isooctyl
Sandy loam	5%	none	none	25%
Heavy clay	20%	none	none	28%
Loam	15%	none	none	20%

Under field conditions, esters of 2,4-D normally hydrolyze to the acid within a few days providing the moisture levels are adequate. It was suggested that because of the relatively rapid hydrolysis of the n-butyl and isopropyl esters in soil, hydrolysis by soil microorganisms is unlikely, and that a soil catalyzed reaction may be responsible for their degradation.

3.3 PERSISTENCE IN WATER

Stream contamination is probably the most important environmental concern in the forest because water is the habitat for many biological species and because water may be utilized downstream for domestic, industrial, and agricultural purposes (25). Norris (25) has made several studies on stream contamination by 2,4-D in western and eastern Oregon. The magnitude of contamination is closely related to the layout of the treatment area with respect to live streams. Areas having a high water table would have the greatest potential to contribute to stream contamination. At most of the sites sampled, concentrations were less than 100 ppb shortly after spraying. These levels were less than 10 ppb after one week.

Data collected by the U.S. Geological Survey program for monitoring pesticides in streams of the western U.S. during the period of October 1966-

September 1968 indicate that 2,4-D was the most frequently found herbicide (26). The maximum concentration found was 0.35 μg/liter (0.35 ppb).

In an aqueous environment 2,4-D will most likely be found in the free anion form (27). Salt formulations dissociate to the anion and esters hydrolyze to the anion, usually within one day. Therefore, the degradation rate of the anion is of primary concern in determining the persistence of 2,4-D in an aquatic environment. Processes which affect 2,4-D persistence in natural waters are microbial degradation, chemical hydrolysis, photodecomposition, volatilization and adsorption. A brief review of these processes follows.

3.3.1 Microbial Degradation

Halter (27) has compiled an extensive review of studies on the persistence of 2,4-D in aquatic environments. In general, laboratory studies show that warm, nutrient rich, 2,4-D-rich conditions favor 2,4-D degradation in water. Therefore, it is reasonable to assume that the cool, nutrient-poor conditions characteristic of many natural surface waters do not promote microbial degradation of the dilute concentrations of 2,4-D likely to be encountered.

Several studies indicate that, even in non-sterile water, 2,4-D will persist if certain microorganisms are absent. Aly and Faust (12), studying the fate of 2,4-D and ester derivatives in natural surface waters, showed that no breakdown of 2,4-D occurred in lake waters aerobically incubated in the laboratory for 120 days. Although esters of 2,4-D were hydrolyzed biologically to 2,4-D acid and the corresponding alcohol within 9 days, only the alcohol moiety was oxidized further. Most of the 2,4-dichlorophenol disappeared within 30 days under aerobic conditions in laboratory tests with natural lake waters, indicating the presence of microorganisms capable of decomposing this compound in natural waters. Under anaerobic conditions, the phenol persisted longer.

Using dilute salts solutions containing 0.1 and 1.0 mg/l 2,4-D, Schwartz (28) showed that no more than 37 percent of the acetic acid moiety disappeared over a period of 3 to 6 months in spite of excellent conditions for biological activity. Since a natural waterway could not be expected to provide as good a microbial environment as the experimental system, it was concluded that 2,4-D would not be substantially degraded by microorganisms in natural waters.

Watson (29) demonstrated that 2,4-D can remain stable in water and mud samples from rivers for up to 6 months depending on the microorganisms, nutrient levels, and suspended sediments.

Other studies have demonstrated that 2,4-D will be degraded in an aquatic environment under more favorable conditions. Studies conducted in warm to temperate water ponds suggest that the majority of 2,4-D persists for a maximum of 30 to 40 days after application; however, 2,4-D probably persists at low ppb levels for several months (27).

3.3.2 Chemical Hydrolysis

Non-enzymatic hydrolysis appears to play a major role in the breakdown of 2,4-D esters to the anion form. Zepp, et al. (30) measured the hydrolysis half-lives of 2,4-D esters at pH 6 and 9, pH levels in the range commonly found in natural waters. The data shown in Table 2 (photolysis and vaporization data shown in the table will be discussed later) indicate a much shorter half-life for all esters at pH 9 than at pH 6. As shown in Table 2, 2-butoxyethyl exhibited the shortest half-life among the 4 formulations tested.

TABLE 2. COMPARISON OF HYDROLYSIS, PHOTOLYSIS, AND VAPORIZATION HALF-LIVES FOR SEVERAL 2,4-D ESTERS AT 25°C*

Ester	Hydrolysis, days		Direct Photolysis,†‡ days	Vaporization,‡ days
	pH 9	pH 6		
Methyl	0.04	44	29	21.7
1-Butyl	0.2	220	--	1.1
1-Octyl	0.2	220	--	11.5
2-Butoxyethyl	0.02	26	16	895

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[*] For water body 1 m deep.

[†] For September in southern United States (lat. 34°N); average value for 1 m deep pure water. Expressed in terms of 12-hr days.

[‡] Calculated for a completely mixed water body.

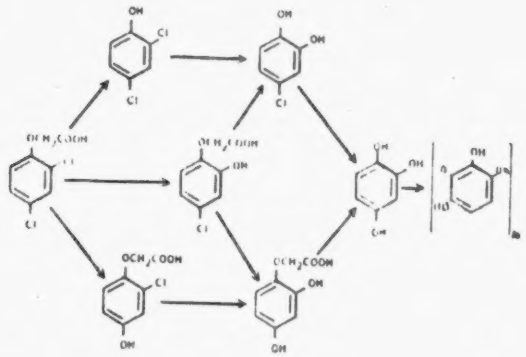
Other results have corroborated the finding that esters undergo rapid hydrolysis at a high pH. Smith (24) studied the hydrolysis of the isopropyl, n-butyl and isooctyl esters of 2,4-D to the free acid in aqueous solutions. At pH 13.0 (0.1 N NaOH) more than 50 percent of all the esters were hydrolyzed in less than one minute. At pH 11.2 (0.1 N Na_2CO_3) the half-lives at 25°C were 5, <5, and 30 minutes for the isopropyl, n-butyl, and isooctyl esters, respectively.

3.3.3 Photodecomposition

Photodecomposition does not appear to be a major mechanism for 2,4-D degradation in surface waters, although some photolysis may occur near the water surface.

Aly and Faust (12) showed that irradiation of aqueous solutions of 2,4-D compounds with uv light from a mercury lamp results in 2,4-D cleavage at the ether linkage and production of 2,4-dichlorophenol. Decomposition was faster at higher pH's. They concluded, however, that photodecomposition in surface waters is not expected to be significant due to the character of natural sunlight (weaker uv radiation) and the presence of suspended and organic matter which reduces the effects of solar radiation.

Crosby and Tutass (31) also studied photodecomposition of 2,4-D in water under uv light and concurred that the major reaction was cleavage at the ether bond to produce 2,4-dichlorophenol. This was subsequently dehalogenated to 4-chlorocatechol; 1,2,4 benzenetriol was then formed and rapidly air oxidized to polyquinoid humic acids. The proposed reaction mechanisms are as shown below.



Irradiations using sunlight appeared to produce degradation products similar to those obtained for irradiation with uv light in the laboratory. 2,4-dichlorophenol and 3-hydroxy-4-chlorophenoxy acetic acid which were identified as degradation products under uv irradiation were also identified as products under sunlight irradiation. 4-chlorocatechol was not identified as a degradation product with sunlight irradiation of 2,4-D esters.

Zepp, et al. (30) carried out laboratory photolysis studies in distilled water, organic solvents, and a natural water sample. In organic solvents, photoreaction involved replacement of a chlorine by hydrogen. In water, at concentrations greater than the solubility (>300 ppm), the major photoproducts were monochlorophenoxyacetic acid esters; in dilute (<1 ppm), air-saturated solutions, the major photoproducts were 2,4-dichlorophenol and compounds resulting from replacement of one chlorine by hydroxyl. In river water, the photoproducts were the same as those in distilled water although more 2,4-dichlorophenol and less hydroxylated phenoxy esters were formed. Photolysis was twice as fast in river water as in distilled water, probably due to photosensitization of substances dissolved in the river water.

Table 2 presents the calculated half-lives for the photolysis of two esters of 2,4-D under the stated conditions. In natural waters, the rate of photolysis will depend on the time of the day, the season, and the latitude. The photolysis would be expected to be greater near the water surface and the half-life to increase with increasing depth due to reduction in light penetration.

3.3.4 Volatilization

Zepp, et al. (30) calculated volatilization half-lives of 2,4-D esters based on the fact that volatilization rates of pesticides from completely mixed water bodies are proportional to their vapor pressures and inversely proportional to their solubilities. The calculated values given in Table 2 indicate that at a pH of 6.0, vaporization may be a more important mechanism for removal of some 2,4-D esters from water than hydrolysis since, at this pH (and perhaps also at lower pH levels) conversion of ester to acid via hydrolysis takes place at a much slower rate. However, at a pH of 9.0, hydrolysis is a more important mechanism for removal of the 2,4-D esters shown in the table.

3.3.5 Adsorption

Halter (27) has reviewed studies on the sorption of 2,4-D to a variety of particles and surfaces found in natural waters. Based on these studies, adsorption does not appear to be a significant factor in the fate of 2,4-D in an aquatic environment.

3.4 FATE IN AIR

Determination of degradation of 2,4-D in air is complicated by the occurrence of airborne losses due to drift and volatilization at the time of application, subsequent vaporization from the treated areas and dispersal into the atmosphere. No studies were found on the actual rate of degradation of 2,4-D in the atmosphere.

A number of researchers have measured quantities of 2,4-D in the atmosphere during the spraying season. These measurements indicate that the levels of 2,4-D in air depend on meteorological conditions and on the formulation used. Farwell, et al. (32), in surveys of airborne 2,4-D in south-central Washington, were unable to correlate 2,4-D application rates with subsequent atmospheric concentrations. Daily samples were taken at 8 stations to determine the average 2,4-D concentration by volatility type. High volatile esters represented the majority of the 2,4-D present in air samples.

Studies on 2,4-D residues in the atmosphere in central and southern Saskatchewan between 1966 and 1975 showed that residues of 2,4-D were present in up to 50 percent of the daily samples collected at any location during the spraying season (33). Atmospheric concentrations were greater for high volatile esters than for low volatile esters. The maximum level of 2,4-D measured was 23.14 $\mu g/m^3$. In any given year and at any of the sampling sites, 10 percent or less of the samples had 2,4-D levels exceeding 1 $\mu g/m^3$.

4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

4.1 PHYTOTOXICITY

A serious hazard in the use of 2,4-D is drift of the herbicide to non-target plants during or after application. Most established grass species are not injured by 2,4-D; however, it is extremely harmful to cotton, grapes, tobacco, beans, tomatoes, fruit trees, and some ornamentals (16). Conifers are susceptible during periods of rapid growth (34).

4.2 TOXICITY TO FISH AND AQUATIC ORGANISMS

Halter (27) has made an extensive review of the literature on the effects of 2,4-D on fish. Acute toxicity of 2,4-D to freshwater fish, as measured in laboratory tests, varies considerably depending on the species used, the water quality, and the 2,4-D formulation tested. Most of the studies have been conducted under laboratory conditions.

The butyl esters of 2,4-D have been found to be 100 times more toxic than their corresponding acids (35). However, under field conditions they are quickly hydrolyzed to the acid or salt. Woodward and Mayer (36) studied acute and chronic toxicity of 2,4-D butyl ester (BE), 2,4-D isooctyl ester (IE), and 2,4-D propylene glycol butyl ether ester (PGBEE) on cutthroat trout and lake trout. Acute toxicity data is presented in Table 3. The 2,4-D BE tended to be slightly more toxic than 2,4-D PGBEE. There was also an increase in susceptibility as temperature decreased. Neither water hardness nor pH significantly influenced toxicity. The 2,4-D IE was not toxic to either species in 96 hours at concentrations less than 60,000 μg/L. In chronic toxicity tests, the no effect concentrations were as follows: for cutthroat trout - 24 μg/L BE and 31 μg/L PGBEE; for lake trout - 33 μg/L BE and 52 μg/L PGBEE.

Meehan, et al. (37) tested acute toxicity of 2,4-D acid, butyl, and isooctyl esters to juvenile salmon, char, and rainbow trout. At concentrations less than 50 ppm, 2,4-D acid produced mortality only in pink salmon fry. The butyl ester was the most toxic, causing nearly complete mortality in all species at concentrations greater than 1.0 ppm. The isooctyl ester was less toxic than the butyl ester.

Folmar (38) reported a 96-hour LC_{50} of 100 mg/L for rainbow trout exposed to 2,4-D DMA salt. Fish were found to avoid 2,4-D at concentrations of 1 mg/L but not at 0.1 mg/L.

Elder, et al. (39) reported that 2,4-D exhibited low toxicity to all freshwater and marine algal species examined at levels approaching the maximum solubility of the herbicide in water. Additional acute toxicity data of various 2,4-D formulations to fish and other aquatic organisms is presented in Table 4.

TABLE 3. ACUTE TOXICITY OF 2,4-D BE AND 2,4-D PGBEE TO FINGERLING CUTTHROAT TROUT AND LAKE TROUT AT DIFFERENT TEMPERATURES (36)

Water Characteristic Chemical and Temperature (°C)	pH	Water Hardness	Cutthroat Trout		Lake Trout	
			96-h LC_{50} (μg/1)	95% Confidence Limits (μg/1)	96-h LC_{50} (μg/1)	95% Confidence Limits (μg/1)
2,4-D BE						
5	7.2	Soft (40 mg/L as $CaCO_3$)	490	397-606	600	541-665
10	7.2	Soft	540	460-640	640	569-720
15	7.2	Soft	770	657-902	820	715-940
2,4-D PGBEE						
5	7.2	Soft	490	400-604	700	631-777
10	7.2	Soft	1,030	920-1,200	630	542-733
15	7.2	Soft	780	663-918	1,000	824-1,210

TABLE 4. ACUTE TOXICITY OF 2,4-D (40)

Formulation	Organism	Dose	Effect	Reference
Butoxyethanol ester	Oyster	3.75 ppm (96 hrs)	50% decrease in shell growth	41
Butoxyethanol ester	Shrimp	1 ppm (48 hrs)	No effect	41
Butoxyethanol ester	Fish (salt water)	5 ppm	48 hr TLm	41
Butoxyethanol ester	Phytoplankton	1 ppm	16% decrease in CO_2 fixation	41
Dimethylamine	Oyster	2 ppm (96 hrs)	No effect on shell growth	41
Dimethylamine	Shrimp	2 ppm (48 hrs)	10% mortality or paralysis	41
Dimethylamine	Fish (salt water)	15 ppm (48 hrs)	No effect	41
Dimethylamine	Phytoplankton	1 ppm (4 hrs)	No effect on CO_2 fixation	41
Ethylhexyl ester	Oyster	5 ppm (96 hrs)	38% decrease in shell growth	41
Ethylhexyl ester	Shrimp	2 ppm (48 hrs)	10% mortality or paralysis	41
Ethylhexyl ester	Fish (salt water)	10 ppm (48 hrs)	No effect	41
Ethylhexyl ester	Phytoplankton	1 ppm (4 hrs)	49% decrease in CO_2 fixation	41
PGBE* ester	Oyster	1 ppm (96 hrs)	39% decrease in shell growth	41
PGBE ester	Shrimp	1 ppm (48 hrs)	No effect	41
PGBE ester	Fish (salt water)	4.5 ppm	48 hr TLm	41
PGBE ester	Phytoplankton	1 ppm (4 hrs)	44% decrease in CO_2 fixation	41
Alkanolamine	Chick	380-765 mg/kg	LD_{50}	42
Isopropyl ester	Rat	700 mg/kg	LD_{50}	42
Isopropyl ester	Chicks	1420 mg/kg	LD_{50}	42

(Continued)

TABLE 4. (Continued)

Formulation	Organism	Dose	Effect	Reference
Isopropyl ester	Guinea pig	550 mg/kg	LD_{50}	42
Butyl ester	Rat	620 mg/kg	LD_{50}	42
Butyl ester	Guinea pig	848 mg/kg	LD_{50}	42
Butyl ester	Chicks	2000 mg/kg	LD_{50}	42
PGBE	Rat	570 mg/kg	LD_{50}	42
Acid	Dog	100 mg/kg	LD_{50}	42
Acid	Chick	541 mg/kg	LD_{50}	42
Dimethylamine	Bluegill	166 ppm	48 hr TLm	43
Alkanolamine	Bluegill	435 ppm	48 hr TLm	43
Isooctyl ester	Bluegill	9 ppm	48 hr TLm	43
Butyl ester	Bluegill	1 ppm	48 hr TLm	43
Isopropyl ester	Bluegill	1 ppm	48 hr TLm	43
PGBE	Bluegill	3 ppm	48 hr TLm	44
Triethanolamine	Swine	50 mg/kg	No effect	45
Triethanolamine	Swine	500 mg/kg	Lethal	45
Butyl ester	Swine	100 mg/kg	No effect	45
Triethanolamine	Chicken	300 mg/kg	No effect	45
Butyl ester	Rat	620 mg/kg	LD_{50}	46
Isopropyl ester	Rat	700 mg/kg	LD_{50}	47
Unspecified amine	Mallard duck	2000 mg/kg	LD_{50}	48
Acid	Pheasant	472 mg/kg	LD_{50}	48
Acid	Mule deer	400-800 mg/kg	LD_{50}	48

[*] PGBE is propylene glycol butyl ether.

4.3 TOXICITY TO INSECTS

There have been some reports of adverse effects to bees from application of 2,4-D, although at normal rates of application there appears to be little hazard to bees or insects from direct toxicity (2). Morton, et al. (52), studying the toxicity of herbicides to honey bees, found that the toxicities of the herbicides studied were relatively unchanged by addition of solvents and surfactants in the formulation process. The formulation of 2,4-D either as an amine or an ester had little influence on its toxicity to honey bees as a stomach poison. No formulation of 2,4-D significantly shortened the half-life of honey bees at concentrations of 10- and 100-ppmw. The butoxyethanol ester of 2,4-D and the amine salt of 2,4-D caused significant reductions in half-life at the 1000-ppmw concentration. When bees were dusted with 2,4-D sodium salt at a dose of 24.17 μg/bee and 2,4-D low volatile oil-soluble ester at a dose of 18.13 μg/bee, mortality was 3.7 percent and 6.4 percent, respectively (53). For comparison with field conditions, an application rate of 1 kg/ha would give a dose of 1.12 μg/bee. Therefore, at recommended application rates, 2,4-D is considered relatively non-toxic to bees.

4.4 TOXICITY TO BIRDS AND MAMMALS

Phenoxy herbicides are generally less toxic to birds than to mammals (34) (also see Table 4). The acute oral LD_{50} for 2,4-D (and 2,4,5-T) ranges from 300 to 5000 mg/kg for poultry, mallards, pheasants, pigeons and quail, with the LC_{50} in bird feed greater than 2500 ppm (34).

Chronic toxicity data is available for various domestic birds and mammals for several 2,4-D formulations and is presented in Table 5. Some of these effects included locomotory disturbance and depressed growth rate. In most cases, however, no effects were observed.

Various studies have also been conducted to provide information on human health hazards of 2,4-D. The 2,4-D isooctyl ester, 2,4-D butyl ester, and 2,4-D isopropyl ester have been found to produce statistically significant higher incidences of congenital malformations in rats or mice (54). Most mutagenesis studies with 2,4-D are negative, although it has been mutagenic in certain test systems (55,56). Further studies are needed to determine carcinogenicity (55,56). In general, reviews of available data

TABLE 5. CHRONIC TOXICITY OF 2,4-D (40)

Formulation	Organism	Dose	Duration	Effect	Reference
Triethanolamine	Swine	50 mg/kg/day	3 doses	None	45
Triethanolamine	Swine	50 mg/kg/day	8-10 doses	Minor transient effects	45
Butyl ester	Swine	50 mg/kg/day	<5 doses	None	45
Triethanolamine	Swine	500 ppm in feed	1 month	Some locomotory disturbance, depressed growth rate, no gross pathology	45
Triethanolamine	Rats	1000 ppm in water	10 months	Depressed growth rate, no gross pathology	45
Triethanolamine	Chicken	1000 ppm in water	Daily production reduced 30%	Egg size normal, from hatching through first 2 months of egg production	45
Alkanolamine	Sheep	100 mg/kg/day	481 days	No effect	49
Alkanolamine	Cattle	50 mg/kg/day	112 days	No effect	49
PGBE ester	Sheep	100 mg/kg/day	481 days	No effect	49
Ethylhexyl ester	Cattle	250 mg/kg/day	14 days	Ill in 3 days, survive & recover from 9 doses. 14 doses lethal.	50
Ethylhexyl ester	Sheep	250 mg/kg/day	17 days	Ill in 3 days, 17 doses lethal	50
Ethylhexyl ester	Sheep & Cattle	100 mg/kg/day	10 days	None to minor effects	50
Not specified	Dog	500 ppm in feed	2 years	None	51

(Continued)

TABLE 5. (Continued)

Formulation	Organism	Dose	Duration	Effect	Reference
Not specified	Rat	1250 ppm in feed	2 years	No effects on growth, survival hermatology or tumor incidence	51
Not specified	Rat	500 ppm in feed	2 years	No effects in reproduction studies	51
Alkanolamine	Chicken	100 mg/kg/day	10 days	No effect on weight gain	49
PGBE ester	Chicken	50 mg/kg/day	10 days	No effect on weight gain	49
PGBE ester	Cattle	100 mg/kg/day	10 days	No effect	49
Acid	Mule deer	80 and 240 mg/kg/day	30 days	Minor symptoms no weight loss	48

indicate that, with the exception of peripheral neuropathy (there have been at least six reported cases of persons being dermally exposed to 2,4-D producing a severe peripheral neuropathy), acute adverse effects of 2,4-D occur only at high doses (55). The oral LD_{50} for humans has been estimated between 80 and 800 mg/kg (55).

4.5 BIOACCUMULATION

The potential for bioaccumulation and persistence of 2,4-D in fish has been the subject of a number of studies. The results of these studies indicate that any 2,4-D accumulated is rapidly broken down to hydrocarbon fragments which are subsequently utilized by the fish for synthesis of the normal body tissue and/or eliminated.

Rodgers and Stalling (57) examined the uptake of the ^{14}C labelled butoxy-ethanol ester of 2,4-D from water by 3 species of fed and fasted fish. The fish were exposed to either 0.3 or 1.0 mg/l for up to 168 hours. The whole body residue, based on ^{14}C measurement, was found to be 7 to 55 times greater than the exposure concentration 1 to 6 hours after exposure. The maximum residue concentrations in fed fish occurred in most of the organs within 1 or 2 hours of exposure; in fasted fish maximum concentrations were observed within 1 to 8 hours of exposure. The maximum residue levels for the fasted fish was 2 to 5 times those for the fed fish. For both the fasted and the fed fish, the herbicide and its metabolites were eliminated rapidly after reaching a maximum concentration.

Shultz (58) exposed fish to varying concentrations of ^{14}C labelled DMA-2,4-D (0.5, 1.0, and 2.0 ppm) for up to 84 days. Radioactive residues, as evidenced by the presence of ^{14}C, were found in all fish tissues and organs analyzed, including the muscle. Analysis of the muscle for 2,4-D, however, indicated less than trace amounts in all but 2 samples out of 30 samples tested, thus indicating that metabolism of 2,4-D had occurred.

Further studies (Stalling and Huckins) (59) on the metabolism of DMA-2,4-D in bluegills showed that residues in fish were not intact 2,4-D. ^{14}C labelled DMA-2,4-D was degraded and ^{14}C was found incorporated into fatty acids, glycogen and protein materials. Since 2,4-D degradation in pools devoid of fish was also observed, it was speculated that the 2,4-D may have been degraded by microorganisms in water and the breakdown products accumulated by fish.

Schultz and Whitney (60) monitored 2,4-D residues in fish, water, and mud following spraying of over 7,000 acres along a canal in the Loxahatchee Wildlife Refuge (Florida). The dodecyl-tetradecyl amine salts of 2,4-D were sprayed at a rate of 4.48 kg/ha. The highest 2,4-D residue in water, 0.037 mg/L, was found on the day following the initial treatment. Among 60 samples of fish, 3 had herbicide residue levels greater than 0.010 mg/kg, 16 had less than 0.010 mg/kg, and the rest had no detectable residues. Florida gallinules had residue levels of 0.30 mg/kg in breast muscle and 0.675 mg/kg in liver one day after spraying but no detectable residues 4 days after spraying.

Numerous studies on the fate of 2,4-D in large animals also indicate that bioaccumulation is not likely to be of concern. In most cases, 2,4-D fed to animals appears to be absorbed readily in the gut and excreted rapidly in urine, largely as unchanged phenoxy acid (2,61).

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Common Name:	Fosamine ammonium
Chemical Name:	Ammonium ethyl carbamoylphosphonate
Major Trade Name:	"Krenite" S Brush Control Agent
Major Applications in Forestry:	Used primarily in Pacific Northwest for woody brush and weed control in site preparation and conifer release. Introductory development work is being conducted in the South for similar use.

SUMMARY

Fosamine ammonium, or "Krenite", is a relatively new herbicide which has been commercially available only in the past few years. The available data on efficacy and environmental fate and impacts are largely from laboratory and field tests with non-forest systems conducted mainly by the manufacturer.

The principal mechanism of fosamine ammonium uptake by plants is through foliage, stems, and buds. In the spring following treatment, bud development is suppressed and susceptible species fail to refoliate or produce miniature, spindly leaves, and die. In soil, fosamine ammonium degrades rapidly via microbial (and to a lesser extent) chemical routes. The major chemical degradation route is hydrolysis to give carbamoylphosphonic acid (CPA), which also degrades rapidly in soil. Fosamine ammonium losses from soil due to volatilization and photodecomposition are not expected to be appreciable. In pasture flora, fosamine ammonium is metabolized to CPA and carboxyphosphonic acid.

Despite its water solubility, fosamine ammonium is a low mobility herbicide. Leaching and desorption from soil are lowest in soils with high clay and heavy metals content. Some fosamine ammonium hydrolysis occurs in water.

Fosamine ammonium is phytotoxic to many non-target woody forest and non-forest species. Pines are the most susceptible conifers, particularly in spring and summer. "Krenite" has low toxicity to fish and to mammals. It is excreted and/or metabolized rapidly by animals and is considered non-bioaccumulable. It is considered non-toxic to soil microorganisms, but has been shown to decrease the rate of nitrification of certain algae.

Non-ionic surfactants which are often added to fosamine ammonium formulations to enhance plant penetration are not considered toxic or hazardous at recommended use rates.

1.0 INTRODUCTION

Fosamine ammonium, or "Krenite", is a herbicide/growth regulant suitable for the control of many undesirable woody plants. It was discovered in 1974 and has been available commercially only in the past few years (1). Species completely controlled include: birch, blackberry, black locust, bracken (fern), loblolly pine, pin cherry, quacking aspen, red alder, red oak, salmonberry, sumac, sweet gum, thimbleberry, vine maple, water oak, white oak, and Virginia pine (2,3,4,5). American elder, eastern cottonwood, eastern white pine, multiflora rose, slippery elm, sycamore, tree-of-heaven, wild grape, and wild plum can be completely controlled with a single foliar application of 2 to 3 gallons of "Krenite" per acre (2). Brush plants partially controlled and suppressed include bigleaf maple, black cherry, blackgum, chokecherry, elm, hawthorn, hickory, persimmon, red maple, sassafras, sourwood, tulip tree (yellow poplar), willow, and white ash (2,6). It does not control evergreen brush (2,7).

Since it is relatively new, commercial application of fosamine ammonium has not been extensive in forestry and it apparently has been used to a greater extent in such other applications as right-of-way and industrial maintenance. In the forest industry, fosamine ammonium is used in the U.S. in reforestation areas and is labelled for conifer release (2,8,9,10) in Washington and Oregon. Data on the extent of use in the region are presented in Table 1 (11). Application rates commonly range from 3 to 12 lb a.i./acre (3/4 to 3 gal product/acre), with lower rates used for conifer release (2). Fosamine ammonium is applied via aerial broadcast with limited ground application reported (4,6). In forestry areas, adequate water is required to obtain best performance (10-40 gallons by air, 50-100 gallons on the ground). Krenite has been used in experimental plots in Maine; limited forestry application has also been reported in the South (8,12,13,14). In the Northeast, fosamine ammonium has been recommended (and apparently used) on Christmas tree stands; the recommended rate is 1-1/2 gallons in 50-100 gallons of water per acre (14). Although no technical support data have been published, in application to the forests in the South, fosamine ammonium has been reported to give similar results when injected versus sprayed on certain species (12).

TABLE 1. AVAILABLE DATA ON "KRENITE" USAGE IN THE PACIFIC NORTHWEST, FISCAL YEARS 1977 TO 1979 (11)

Agency	F.Y.	Targets	Units Treated	Amount Used
State of Washington, Dept. of Natural Resources	1978	Forestry and non-forestry	659 acres	517 gallons
	1977	Forestry and non-forestry	---	425 gallons
State of Oregon, State and Private Usage	1979	Brush road maintenance	166 miles	20 pounds
State of Oregon, Bureau of Land Management	1979	Brush/conifer release	809 acres	809 pounds
	1979	Site preparation and conifer release	643 acres	3585 pounds
State of Oregon, Permittee/grantee	1979	Broadleaf road maintenance	26 acres	104 pounds
USDA Region 6, Oregon and Washington	1978	Site preparation	960 pounds	310 acres
	1978	Right-of-way maintenance	506 pounds	82 acres
	1978	Right-of-way maintenance	12 pounds	2 acres

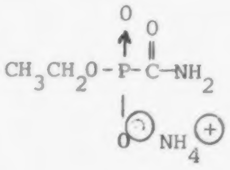
Fosamine ammonium is also registered as a foliar spray for control of field bindweed and brush control on rights-of-way, industrial sites, storage areas, drainage ditch banks, railroad, utilities, and lands adjacent to and surrounding domestic water supply reservoirs, supply streams, lakes, and ponds (2,3,12,15). Usual application rates are 6 to 12 lbs/acre on rights-of-way (4), and application methods include aerial broadcast methods or ground methods (4,16).

Fosamine ammonium is usually applied in the late summer or early fall before leaf coloration occurs; it is quickly absorbed by the plant foliage, stems and buds (3,6). Browning of the leaves occurs soon after application in non-deciduous species; no such immediate impact is observed in deciduous species. In the spring following treatment, bud development is suppressed in all susceptible species which fail to refoliate and die. However, the stems of many woody species may remain alive for 1 to 3 years following application of fosamine ammonium.

Fosamine ammonium is marketed domestically by E.I. DuPont de Nemours Co., Inc. (15). It is available as the amber-colored water soluble liquid formulation containing 41.5 percent (4 lb. minimum/gallon) active ingredient (15) and is marketed in 1-, 5-, and 30-gallon drums (2,3). Non-ionic surfactants such as DuPont Surfactant WK, Tween 20, or Triton X-100 are often added at a rate of 1 quart per 100 gallons prior to application to promote plant penetration (16,17).

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The active ingredient is ammonium ethyl carbamoylphosphonate:



$$CH_3CH_2O-\underset{O^{\ominus}\ NH_4^{\oplus}}{\underset{|}{\overset{O}{\overset{\uparrow}{P}}}}-\overset{O}{\overset{\|}{C}}-NH_2$$

It is a white crystalline solid melting at 175°C. It is highly water soluble (179 g/100 g) and slightly soluble in most common organic solvents as indicated below (15,18):

Solvent	Solubility, g/100 g at 25°C
Chloroform	0.004
n-Hexane	0.02
Acetone	0.03
Benzene	0.04
Dimethylformamide	0.14
Ethanol	1.20
Methanol	15.80

Fosamine ammonium has low volatility, with a vapor pressure of 4×10^{-6} mm Hg at 25°C (18).

3.0 ENVIRONMENTAL FATE

Very little environmental fate data have been published in connection with the use of fosamine ammonium in forests. Most of the discussion in this section is based on data reported for non-forest applications.

3.1 UPTAKE AND METABOLISM IN PLANTS

Limited studies have been, and are being, conducted on the uptake of fosamine ammonium in plants (2). The studies indicate that it is absorbed by foliage, buds and stems with no major visible effect until the following spring when bud development is either prevented or severely limited by the production of only miniature, spindly leaves which are chlorotic and do not photosynthesize adequately (18). (As noted previously, certain non-deciduous plants such as bindweed and some pines may show browning immediately after application.) (3,18).

In uptake, translocation and fate studies in greenhouse experiments with apple seedlings using ^{14}C-labelled fosamine ammonium, slow penetration and a half-life for the intact material of 2-3 weeks were observed when fosamine ammonium was applied to leaves; better penetration occurred when the fosamine ammonium was applied to the stems (18). The use of surfactant greatly enhanced fosamine ammonium penetration. Once absorbed, foliar-applied fosamine ammonium rapidly translocated into all leaves, stems and roots. When applied to the roots via nutrient solution, fosamine ammonium also translocated rapidly to all parts of the plants. Field studies of fosamine ammonium efficacy have indicated that complete coverage of all parts of the woody plants is necessary for effective control under practical use situations (18).

Limited data are available on the mechanism and products of metabolic degradation of fosamine ammonium in plants. The metabolism of ^{14}C-labelled "Krenite" has been studied at 12 lbs a.i./acre on a pasture area consisting of a small pin oak surrounded by grass and clover. Fosamine ammonium had an average half-life of 7 days in the pasture flora. The only metabolites found were carbamoylphosphonic acid (CPA) and carboxyphosphonic acid which reached a maximum concentration after two weeks, then rapidly degraded. Twelve months after treatment, no fosamine ammonium, CPA, or carboxyphosphonic acid (<0.05 ppm) were found in pasture turf (19).

3.2 FATE IN SOIL

The fate of fosamine ammonium in soil can be described in terms of 6 factors: volatilization, photodecomposition, adsorption/leaching, runoff, and chemical and microbial degradation. Based on limited field data, volatilization and photodecomposition are not significant contributors to the loss of fosamine ammonium following application (2,20).

3.2.1 Adsorption, Leaching and Runoff

Fosamine ammonium is generally considered a low mobility herbicide (3, 20). It is rapidly and reversibly adsorbed on soil particles. On Keyport silt loam soil, fosamine ammonium has a Freundlich K equilibrium constant of greater than 20, indicating a high adsorption to the soil (3). The extent of adsorption (and desorption) is a function of soil type as well as temperature, moisture and pH. Because of its ionic character, fosamine ammonium is more strongly adsorbed to soils high in clay and heavy metals content than to other soils (21). No quantitative data are available on the effects of soil organic matter, temperature, moisture and pH on fosamine ammonium.

The adsorption capacity of a given soil type for fosamine ammonium affects the potential for leaching of the herbicide from soil. The leaching tendency would be lower with those soil types and under those conditions which promote adsorption. Based on limited data available, it appears that leaching is less pronounced in soils with high clay and heavy metals content than in soils with lower clay and heavy metals content. Tables 2 and 3 present the results of laboratory leaching tests with silt loam Keyport soil (17 percent clay content) and sandy loam Fallsington soil (12 percent clay content). The data indicate low leaching tendencies for both soils, but higher leaching for the soil with the lower clay content. The mobility of fosamine ammonium in soil has been investigated under simulated rainfall conditions. Table 4 presents the results of a laboratory leaching study with Fallsington soil in flats 12 x 36 x 3 in., sloped 5 to 10 degrees under a "rain" application of 25 to 50 ml over a 2-hour period. "Krenite" (15 lb a.i./acre) was applied to the top third of the flat before "rain" was applied.

As shown in Table 4, most of the "Krenite" remained near the surface and in the upper portion of the flat, thus indicating no appreciable downward or lateral mobility. This conclusion has been also confirmed in a field study (20). Other field studies conducted in Florida, Delaware, and Illinois with ^{14}C-labelled fosamine ammonium have also indicated very little or no downward movement in soil of the herbicide or its degradation products (1,18).

TABLE 2. SHORT TERM LABORATORY LEACHING STUDY WITH ^{14}C-LABELLED FOSAMINE AMMONIUM (1,20)

Soil Section *	Activity Recovered, %	
	Keyport Soil	Fallsington Soil
0 - 2 inch	43.5	27.3
2 - 4 inch	21.5	34.6
4 - 8 inch	10.5	13.7
8 - 12 inch	3.2	9.5
Total in Soil	78.7	85.1
Total in Leachate	4.4	9.3
Total Recovered	83.1	94.3

*Columns, 2 inches by 10 inches in length, were packed with soil, Krenite was added to the top of the column and water (rate not given) was applied until 29 inches passed through the columns; Fallsington time 7 days, Keyport time 20 days.

The role of organic matter in the soil on adsorption and mobility of fosamine ammonium have not been studied and no actual measurements of these parameters in the forest soil have been reported.

Because of its low mobility and its strong adsorption to soil particles, loss of fosamine ammonium via solubilization or subsurface leachate would be expected to be minimal. Loss in surface runoff of fosamine ammonium from soil surface, however, is possible via mobilization of fosamine ammonium-adsorbed soil particles by the action of flowing surface water, especially following a heavy rainfall.

TABLE 3. LONGER-TERM LABORATORY LEACHING STUDY WITH ^{14}C-LABELLED FOSAMINE AMMONIUM (1,20)

Soil Section*	Activity Recovered, %	
	Keyport Soil	Fallsington Soil
0 - 2 inch	49.6	37.7
2 - 4 inch	22.0	34.8
4 - 8 inch	5.8	11.3
8 - 12 inch	3.9	6.1
Total in Soil	81.3	89.9
Total in Leachate	2.0 or less	2.0 or less
Total Recovered	83.3	91.9

*Columns 2" by 12" in length were packed with soil and then 100 gm of soil treated with ^{14}C fosamine ammonium were added to the top of each column. After aging for 30 days, water was added at a constant rate of 0.5 inches per day, for 45 days.

TABLE 4. LABORATORY MOBILITY STUDY USING ^{14}C LABELLED FOSAMINE AMMONIUM (20)

Soil Layer	Activity Recovered (%) in Increments Along Flat		
	0 - 12 inch	12 - 24 inch	24 - 36 inch
First inch	92.6	--	--
Second inch	1.0	--	--
Third inch	0.2	--	--
Total	93.8	2.08	0.33

3.2.2 Chemical and Microbial Degradation

Fosamine ammonium is not considered a persistent compound in soils. Under field conditions in Florida, Illinois and Delaware, the half-life of ^{14}C-labelled fosamine ammonium in soils was approximately one week following treatment at an application of 11.3 kg/ha (a rate typical of practical use levels) (1). The results, shown in Table 5, indicate that fosamine ammonium and its major metabolite carbamoylphosphonic acid (CPA) had disappeared completely within 3 to 6 months. Much of the residual ^{14}C was incorporated into the soil organic matter (alpha-humus, beta-humus, soluble humin fractions, etc.). Greenhouse soil studies with ^{14}C-labelled fosamine ammonium indicated a half-life of about 10 days, which is in good agreement with the field study half-life (1,18).

TABLE 5. C RESIDUES FOUND IN 0-5 cm SOIL INCREMENTS IN FIELD STUDIES (1)

Time After Application	Percentage Detected ^{14}C in			Percentage Detected ^{14}C as	
	H_2O Extract†	pH 10 Extract	Unextracted Residue	Fosamine	CPA
KEYPORT SILT LOAM*					
0 day	68.3	29.1	3.1	>96	<1
1 week	32.8	61.0	6.1	49.3	<1
2 week	27.3	64.0	8.2	27.5	26.7
6 week	20.8	69.3	8.9	5.6	10.4
6 month	18.7	70.1	9.0	<1	<1
1 year	3.8	82.5	9.2	<1	<1
FLANAGAN SILT LOAM*					
0 week	73.0	19.6	1.8	>95	<1
1 week	52.0	34.9	2.6	40	5
6 week	50.1	36.7	5.5	<1	40
2.5 month	31.2	55.5	8.8	<1	<1
3.5 month	21.7	62.4	8.1	<1	<1
6 month	20.9	63.2	8.0	<1	<1
10 month	20.1	62.2	8.3	<1	<1
12 month	18.5	61.7	8.5	<1	<1
LEON IMMOKALEE FINE SAND*					
0 week	90.5	4.4	1.1	>95	<1
1 week	70.1	8.3	1.8	36	60
2 week	64.0	9.5	3.7	<5	83
1 month	47.3	38.0	3.9	<1	41
3 month	35.7	48.9	4.2	<1	<1
6 month	34.1	52.3	4.1	<1	<1
9 month	29.6	54.4	4.4	<1	<1
12 month	28.7	52.2	4.0	<1	<1

*See Table 6 for soil property data.

†CPA was major constituent in the water extract.

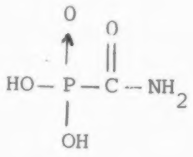
TABLE 6. PROPERTIES OF SOILS USED IN FOSAMINE AMMONIUM PERSISTENCE STUDY SHOWN IN TABLE 5

	Constituents, %				
SOIL	SAND	SILT	CLAY	ORGANIC MATTER	pH
Keyport silt loam, Newark, Delaware	21	62	17	2.8	6.4
Flanagan silt loam, Rochelle, Illinois	5	64	31	4.0	5.0
Leon Immokalee Fine Sand, Bradenton, Florida	99	0	0	1.0	6.4

As described below, fosamine ammonium degradation in soil occurs via both chemical and microbial routes.

Chemical Degradation--

Hydrolysis of fosamine ammonium to carbamoylphosphonic acid (CPA) is thought to be one of the major chemical degradation routes in soil (1,18).



$$HO-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle O}{\overset{\uparrow}{P}}}}-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2$$

CPA

The kinetics of and pH's favorable to hydrolysis have not been determined. Like fosamine ammonium, CPA is non-volatile and degrades fairly rapidly in soils (see above). The dependence of the degradation of CPA in soil on soil type, temperature, moisture and pH have not been determined.

Microbial Degradation--

Laboratory studies by Han (1) have shown that fosamine ammonium is decomposed quickly by soil microorganisms. When ^{14}C-labelled fosamine ammonium was added to Fallsington sandy loam and Keyport silt loam soils in laboratory biometer flasks to establish 4 and 20 ppm treatment levels, between 45 and 75 percent of the original weight of the labelled carbon was evolved as CO_2 within 90 days (1). As noted in Figures 1 and 2, the degradation was essentially nil in the sterile soils at least during the first 20 to 30 days of the experiments; the minimal activity noted subsequently in these soils is probably due to the loss of complete sterility.

The effects of soil moisture, temperature, pH, soil type and nutrient levels on microbial degradation of fosamine ammonium have not been studied. Also not evaluated is the mechanism of degradation of fosamine ammonium by soil microorganisms.

3.3 PERSISTENCE IN WATER

Several laboratory studies have been conducted by DuPont [Han (1)] on fosamine ammonium persistence and degradation in water. Aqueous solutions of ^{14}C-labelled fosamine ammonium at 5 ppm concentration were found to be stable in the dark (less than 3 percent decomposition) for 4 weeks at pH 7 and 9, but at pH 5 hydrolyzed nearly completely to CPA within 2 weeks (1). The half-life for the reaction at pH 5 was approximately 10 days. At 7200 ppm concentration, which is more typical of normal spraying operations, less than 3 percent decomposition was observed at any of the pH's studied. According to Han (1), decomposition under actual field conditions is expected to be minimal.

The rate of fosamine ammonium photodecomposition in water is extremely slow, as measured under laboratory conditions, and is not expected to be significant in the environment (1,20). Laboratory photolysis studies conducted with a General Electric-40BL lamp (300-500 nm) positioned 7 inches from the surface of the samples containing 5 ppm fosamine ammonium and with an irradiation intensity of 1200 watts/sq cm (about half of the intensity of the sun at noon) indicated only 2 percent decomposition of fosamine ammonium in 8 weeks (1,18). Aqueous fosamine ammonium samples (5 ppm at pH 5) exposed to direct July sunlight in Wilmington, Delaware, showed very minor degradation after 4 weeks (1).

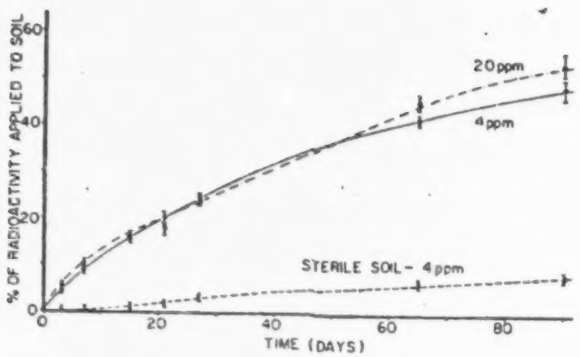


Figure 1. $^{14}CO_2$ Evolved From ^{14}C Fosamine Ammonium Treated Fallsington Sandy Loam in Biometer Flasks (1)

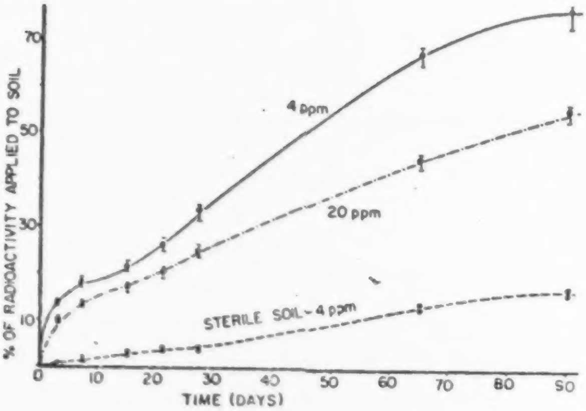


Figure 2. $^{14}CO_2$ Evolved From ^{14}C Fosamine Ammonium Treated Keyport Silt Loam in Biometer Flasks (1)

4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

4.1 PLANTS

Fosamine ammonium is considered phytotoxic to most non-target woody forest and non-forest plants (18,22,23). Pines are the conifers most susceptible to injury from fosamine ammonium. In a study by Radosevich, et al. (24) on the seasonal tolerance of 6 coniferous species to fosamine ammonium, it was determined that conifers were more tolerant after fall dormancy, but substantial injury and mortality occurred in spring or summer, when rates of photosynthesis were high and moisture stress was low. The actual results of the study are summarized in Table 7.

Since fosamine ammonium is rapidly degraded in the soil, there should not be sufficient residue carry-over to cause injury to susceptible species in the next growing season.

TABLE 7. SURVIVAL OF SIX CONIFEROUS SPECIES FOLLOWING FOSAMINE AMMONIUM APPLICATION (24) (4.5 kg/ha)

Conifer Survival (% of untreated)				
	Application Date			
Species	April 14	July 7	September 23	Average
Ponderosa pine	0	0	96	32
Jeffrey pine	4	6	80	30
Sugar pine	14	45	85	55
Douglas fir	4	12	94	37
White fir	6	17	88	37
Red fir	3	29	97	43

4.2 FISH

Limited studies conducted on the toxicity of fosamine ammonium to fish indicate it has a low toxicity to several species (25). LC_{50}'s of "Krenite" for bluegills, rainbow trout, and fathead minnows are 670, >1000, and >1000 ppm, respectively (2,18). The 48-hour LC_{50} in Daphnia magna is 1,524 ppm. The 96-hour LC_{50} on salmon is 8,290 ppm in a static bioassay and 9.812 ppm in a replacement bioassay (2). No data are available on the metabolism of fosamine ammonium in these species or in fish.

4.2 WILDLIFE

"Krenite" has low toxicity to warm-blooded animals. The acute oral LD_{50} of "Krenite" for rats is 24,000 mg/kg; for guinea pigs, 7,380 mg/kg (26). The approximate lethal dose for dogs is greater than 15,000 mg/kg (2). Little data are available in the literature on toxicities of fosamine ammonium to birds and wildlife species (i.e., deer, beaver, etc.). However, a toxicological investigation conducted on mallard ducks and bobwhite quail showed "Krenite" to have very low toxicity to these species (LD_{50} greater than 10,000 mg/kg for both species) (18,26). Subacute oral toxicity studies conducted on rats showed no adverse effects except for mild diarrhea from feeding 2,200 mg/kg/day over a 2-week period. A level of 1,000 ppm in the rat diet for 3 months also showed no adverse effects except for diarrhea (2). At high doses (up to 10,000 ppm), rats had kidney tubule cell swelling and dogs had increased heart and stomach weights (5). In dietary studies conducted on dogs for 6 months and sheep for 3 months, little evidence of toxicity was found (2,18). Acute dermal toxicological investigations using rabbits gave an LC_{50} of greater than 4,000 mg/kg (27). Other studies have indicated "Krenite" has a relatively low acute inhalation toxicity (28). A teratology study indicated that fosamine ammonium was not teratogenic when pregnant rats were fed 10,000 ppm in the diet. When rats were fed at the rate of 5,000 to 10,000 ppm, there was no adverse effect on reproduction. In an Ames test, fosamine ammonium was not mutagenic either with or without activation (2).

Fosamine ammonium is considered non-toxic to fauna, and is registered for use along stream banks and other water impoundments (9).

4.4 BENEFICIAL INSECTS

Fosamine ammonium is considered non-toxic to bees. A 10,000 ppm spray solution produced no greater mortality than that presentamong untreated controls (2).

4.5 MICROFLORA

Fosamine ammonium is considered non-toxic to soil microorganisms. Laboratory studies using 3 agricultural soils (Leon Immokalee fine sand from Bradenton, Florida; Fallsington sandy loam from Glasgow, Delaware; and Flanagan silt loam from Rochelle, Illinois) showed that populations and species of soil bacteria and fungi were unaltered over an 8-week period after treatment with 10 ppm fosamine ammonium (20). In an agar plate bioassay test, fosamine ammonium showed little or no fungitoxicity at treatment rates up to 100 ppm. The fungi tested were: Aspergillus niger, A. Terreus, Penicillium citrinum, Gibberella saubinetti, Fusarium sp., Alternaria sp., Rhizoctonia solani, and Pythium sp.

Several studies have been conducted on the effects of fosamine ammonium on the activity of various soil microorganisms, with varying results. In laboratory studies using 2 soils (Fallsington sandy loam and Keyport silt loam), no effect could be detected on either the population or activities of soil nitrifying bacteria during a 5-week test period after application of 0.5, 5, and 20 ppm fosamine ammonium (1,20,29). However, results of a laboratory study by Hallborn and Bergen (30) showed that treatment of Nostoc sp. algae isolated from Peltigira pratextata lichen with 100 ppm "Krenite" drastically decreased nitrogen fixation rates, with total inhibition occurring after 8 hours.

4.6 BIOACCUMULATION

Fosamine ammonium is metabolized and/or excreted rapidly by animals and is considered non-bioaccumulable (17). When ^{14}C-labelled fosamine ammonium was administered as a single oral dose to preconditioned rats by intragastric intubation, the radioactivity was rapidly eliminated in the feces (87 percent) and urine (13 percent) (31). Trace amounts of radioactivity were found in the gastrointestinal tract, hide, and exhaled air (0.1-0.2 percent). Less than 0.05 percent radioactivity was found in the body tissues after 72 hours. Total recovery of applied radioactivity was nearly 100 percent. The eliminated carbon-14 in both urine and feces was 87 percent intact fosamine ammonium and about 13 percent carbamoylphosphonic acid (CPA). The degradation of fosamine ammonium to CPA is consistent with known metabolic pathways of organophosphorous agrichemicals in animals (32).

In addition, when a lactating nanny goat was given seven consecutive daily doses of ^{14}C fosamine ammonium, the radioactivity was again rapidly eliminated in the feces (88.6 percent) and the urine (9 percent). Total ^{14}C residues of fosamine ammonium and its metabolite, CPA, in all tissue and organs were less than 0.05 ppm 24 hours after the last dose (19).

Fosamine ammonium and its soil degradation products do not significantly accumulate in fish. In a laboratory study on catfish exposed to 1 ppm fosamine ammonium for 4 weeks, the accumulation factor was less than 1 and 50 percent of these residues were eliminated in a two-week withdrawal period (20,33).

There is no evidence for bioaccumulation of fosamine ammonium in microorganisms.

5.0 MISCELLANEOUS

As indicated in Section 1.0, non-ionic surfactants such as DuPont Surfactant WK, Tween 20, or Triton X-100 are often added to fosamine ammonium spray formulations to promote plant penetration. Based on data supplied by the manufacturer and OSHA "data sheets", these surfactants are not considered toxic or hazardous.

There are indications in the literature that fosamine ammonium is unsuitable for killing and dessicating shrubs to prepare brushfield for burning before reforestation in the Pacific Northwest (22). In the Coast ranges of Oregon and Washington, foresters prefer to spray brush for site preparation during late winter or early spring and burn the dry bush in August or September of the same year. Since fosamine ammonium is most effective when applied during late summer or early fall and does not show its effects on plants until the following spring, burning may not be possible until at least 1 or even 2 years after spraying. This disadvantage limits the usefulness of fosamine ammonium for preburn dessication, especially in the Coast Ranges of the Pacific Northwest.

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Common Name:	Glyphosate
Chemical Name:	N-(phosphonomethyl)glycine
Major Trade Name:	Roundup
Major Applications in Forestry:	Glyphosate is used for site preparation, conifer release, post directed sprays, and tree injection.

SUMMARY

Being a relatively new pesticide, the environmental fate and potential ecological effects of the use of glyphosate in forests have not yet been adequately studied. The limited data which are currently available are almost entirely from greenhouse and laboratory studies with agricultural systems and laboratory animals and have been largely generated by the manufacturer. These data indicate high effectiveness, short persistence in soil and water environments, and very low toxicity to animals for glyphosate. Because of these features, a great potential exists for future large-scale use of glyphosate in forestry.

Glyphosate is absorbed almost exclusively via plant foliage and is translocated throughout the plant. Less than one percent of the glyphosate in the soil is absorbed via the roots. Glyphosate is apparently not metabolized to a significant degree in plants and its mode of action is believed to involve inhibition of aromatic amino acid synthesis. It is rapidly and strongly adsorbed to soil particles; this strong adsorption by soil accounts for the observed lack of mobility and leaching tendency of glyphosate in soil and its "unavailability" for root uptake. Adsorption to soil is believed to be through the phosphonic acid moiety, since phosphate level in the soil influences the quantity of glyphosate adsorbed and glyphosate adsorption is greater in soils saturated with Al^{+++} and Fe^{+++} than with Na^{+} and Ca^{++}.

Dissipation of glyphosate in soil is fairly rapid (half life about 2 months) and is primarily due to microbial degradation. The principal soil metabolite of glyphosate is aminomethylphosphonic acid (AMPA), which itself is also highly biodegradable. Glyphosate is subject to biodegradation in natural waters and has an estimated half-life of 7 to 10 weeks.

Under normal application rates, Roundup® herbicide (the commercial formulation of glyphosate) should not be toxic to forest fauna at recommended application rates. Bioassay tests on several aquatic invertebrates and fishes have indicated 96-hr LC_{50} values ranging from 2.3 mg/L for fathead minnows to 43 mg/L for mature scuds. Aquatic tests comparing toxicities of the technical grade glyphosate, Roundup herbicide and the surfactant used in Roundup herbicide have indicated that the surfactant and not the glyphosate is the primary toxic agent in Roundup. Animal feeding studies with glyphosate have indicated low toxicity to rat, mallard duck and quail and little or no potential for bioaccumulation.

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1.0 INTRODUCTION

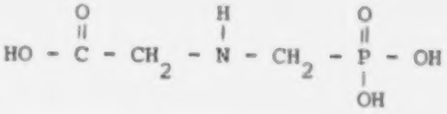
Glyphosate is a broad-spectrum and relatively non-selective herbicide introduced in 1971 (1). Its primary uses are in agriculture and on non-crop areas such as industrial and recreational areas, irrigation canals and rights-of-way (2). The use of glyphosate in forestry is relatively new and has been primarily in the Pacific Northwest for control of brush species such as bigleaf maple, vine maple, alder, salmonberry, thimbleberry, hazel, and bracken fern (3). Specific forestry applications include preplant nursery uses for pine seedlings, site preparation, and conifer release and seed orchards and seed production areas (4). In 1979, approximately 4100 lb of glyphosate was used in U.S. Forest Service Regions 5 and 6 (more specifically, in the Pacific Northwest); of this, about 3600 lb were used for conifer release, and the remainder was used for general weed control, including right-of-way applications (5). According to the Oregon Department of Forestry (6), use of glyphosate is now an integral part of that state's vegetation management; about 3000 to 5000 acres of state-owned forest land are annually treated with glyphosate, primarily for conifer release. In the Pacific Northwest, glyphosate has proved considerably more effective than 2,4,5-T for the control of certain specific weed species (e.g., salmonberry and thimbleberry). For these applications, glyphosate may be overall more cost-effective than 2,4,5-T, despite its higher per acre treatment cost (estimated at about $50/acre). No quantitative data are available on the extent of usage of glyphosate by private timber companies, although such uses are reported to be "major" (3). Limited uses of glyphosate have also been reported in the northeastern United States, primarily in connection with Christmas tree production and in experimental site preparation/conifer release plots. In Maine, 6,000 lb of glyphosate were used for these purposes in 1979, and Georgia Pacific treated 2,400 acres of its forest plantation in Maine with glyphosate in 1979 (8).

Both ground and aerial application methods have been used in connection with forestry uses. When applied aerially, use of "raindrop" nozzles significantly reduces potential for drift. A typical application rate for conifer release is 1 to 1.5 quarts of Roundup herbicide per 10 gallons of solution per acre; somewhat higher rates (about 3-4 quarts of Roundup herbicide per 10 gallons of solution) have been used for site preparation (6).

Glyphosate is manufactured by Monsanto Co. and the commercial formulation, Roundup®, is a mixture containing a surfactant and the isopropylamine salt of glyphosate (24). The role of the surfactant is to increase absorption and translocation of the herbicide in plants.

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

Glyphosate is the common name for N-(phosphonomethyl)glycine. Its structural formulation is:



$$HO - \overset{\overset{O}{\parallel}}{C} - CH_2 - \overset{\overset{H}{|}}{N} - CH_2 - \underset{\underset{OH}{|}}{\overset{\overset{O}{\parallel}}{P}} - OH$$

It is a white odorless solid with a melting point of 200°C. The solubility in water is 1.2 percent at 25°C and the solubility in other solvents is reported as "none" (11). The vapor pressure of glyphosate is reported as "negligible".

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM BY PLANTS

Field and greenhouse studies have indicated that the basic mechanism for the uptake of glyphosate is through the plant foliage; some root uptake may also take place, depending on the soil type. Although the mechanism of glyphosate action is not fully elucidated, it is believed to involve blockage of aromatic amino acid biosynthesis (12).

Humidity and the presence of surfactants significantly increase the absorption of glyphosate by the foliage. Foliar absorption experiments conducted in a greenhouse by Gottrup, et al. (13), using Canada thistle (*Cirsium arvense*) and leafy spurge (*Euphorbia esula*) indicated maximum absorption under conditions of high humidity when glyphosate was applied with surfactant. Under conditions of low relative humidity (ambient glasshouse conditions), each species absorbed about 27 percent of the applied herbicide after one week. Under high relative humidity (plants in plastic bags), absorption was about 85 percent after one week. Both low and high humidity experiments were conducted in the presence of surfactants.

Wyrill and Burnside (14) also conducted foliar absorption experiments on field and greenhouse plants. Tests were conducted on common milkweed

(Asclepias syriaca) and hemp dogbane (Apocynum cannabinum). The tests found that neither wax removal, subcuticular cell damage, nor surfactant significantly increased diffusion of glyphosate across common milkweed or dogbane cuticles. Removal of epicuticular wax with chloroform did not appreciably increase absorption of glyphosate in either species.

The hydrophobic epicuticular wax is probably an effective barrier to the polar, negatively charged glyphosate molecule. However, since wax removal had little effect on glyphosate absorption, it appears that the cuticle is also an effective barrier to glyphosate absorption. Wyrill and Burnside (14) noted that this was possibly because glyphosate was repelled by negatively charged cuticle components. Based on the finding that an effective surfactant did not increase glyphosate diffusion across the cuticles of either species, Wyrill and Burnside (14) postulated that the main influence of the surfactant may be on the plasma membrane and not the leaf cuticle.

Sprankle, et al. (15) investigated the absorption of glyphosate via roots. Greenhouse studies found that soybean and corn grown in Spinks sandy loam soil absorbed less than 0.8 percent of the glyphosate applied to the soil. However, glyphosate was readily absorbed from a nutrient solution by wheat seedlings. This suggests that the absence of glyphosate effect when applied to the soil is probably due to the unavailability of glyphosphate in soil for absorption by the roots (see Section 3.2.1) (15).

Once absorbed by plants, glyphosate is translocated to all plant parts including the underground propagules of perennial species, thus preventing their regrowth (11). Studies of the metabolism of glyphosphate by Canada thistle, leafy spurge, milkweed and hemp dogbane have indicated no significant degradation in these plants up to 20 days after treatment (13,14). No data have been reported on persistence in plants over longer time periods. In one study using ^{14}C-glyphosate on Canada thistle and leafy spurge foliage and roots, the examination of autoradiographs of thin layer plates containing plant extracts indicated the presence of intact ^{14}C-glyphosate in both species with no detectable amount of metabolites of ^{14}C-glyphosate one week after treatment (13).

3.2 FATE IN SOIL

Dissipation of glyphosate in soil is considered to be relatively rapid.

Rueppel, et al. (10) conducted greenhouse soil dissipation studies in which glyphosate was applied to soil just prior to the planting of corn. Three different soil types (Drummer silty clay loam, Norfolk sandy loam, and Ray silt loam; organic contents: 6 percent, 1.0 percent, and 1.0 percent, respectively) and two different glyphosate concentrations (4 and 8 ppm corresponding to approximately 4.48 and 8.98 kg/ha application rates) were used. For both application rates, the calculated half-lives were 3, 130, and 27 days for Drummer, Norfolk, and Ray soils, respectively. The relatively rapid dissipation of glyphosate in soil has been substantiated by the results of actual field studies (conducted by Monsanto on eleven different soils covering a full range of soil types and geographic areas) which indicate an average half-life of 2 months. Other investigators have reported half-lives of 17 to 19 weeks for sandy soil and 3 weeks in silt loam (16).

Adsorption on soil particles, which influences the potential for leaching, runoff, and degradation by the action of soil microorganisms are the primary factors in determining the dissipation of glyphosate from soil. Photodecomposition, volatilization and chemical degradation do not appear to make significant contributions to glyphosate losses. (As noted in Section 2, glyphosate is reported to have a negligible vapor pressure. Rueppel, et al. (10) investigated the photodecomposition of ^{14}C-glyphosate in solution using a Crosby photoreactor and found no loss of ^{14}C content via volatile degradation products and no change in the composition of the test solution.)

3.2.1 Adsorption, Leaching and Runoff

The strong adsorption of glyphosate on soil has been demonstrated in a number of studies and is considered the initial step in inactivation (i.e., "unavailability" to plant roots) of glyphosate in soil. In a greenhouse study, Sprankle, et al. (15) measured the effect of glyphosate on the growth of 16-day-old wheat plants grown on washed quartz sand, clay loam (3.7 percent organic content) and muck soil (81 percent organic content) treated with glyphosate at application rates of 4.5, 11, and 56 kg/ha. While no reduction in plant yield was observed for the two soils, glyphosate treatment significantly reduced plant growth in the quartz sand, thus indicating that the herbicide was adsorbed to the soils and that adsorption to sand was much less extensive.

Sprankle, et al. (15) also studied the effect of pH and phosphate on the adsorption of glyphosate by soil, using plant yield as a measure of glyphosate inactivation and, hence, adsorption. While no significant pH effect was observed at glyphosate application rates of 4.5 and 11 kg/ha, a pronounced effect was observed at an application rate of 56 kg/ha; at this rate, reductions in yield of 20 percent, 7.5 percent, 27 percent, 51 percent and 55 percent were observed at pH levels of 4.6, 5.1, 5.6, 6.1 and 6.7, respectively (see Table 3). These results indicated a decrease in glyphosate adsorption as the pH was raised. Binding of glyphosate to soil was also determined to be influenced by phosphate. Glyphosate applied at 11.2 kg/ha with 98 kg/ha of phosphate gave a significant reduction in plant dry weight, while 11.2 kg/ha of the herbicide alone had no effect. The data also indicated that the initial glyphosate binding was reversible with phosphate anions competing with glyphosate for binding sites.

Glyphosate adsorption to the soil begins immediately after application and increases slowly after one hour (17). Glyphosate rapidly binds to kaolinite, illite and bentonite clays and to muck. Fe^{+++} and Al^{+++} saturated clays and organic matter adsorb more glyphosate than Na^{+} or Ca^{++} saturated clays and organic matter. Based on these observations and the fact that the phosphate level in the soil is the most important factor in determining the quantity of glyphosate adsorbed, it has been concluded that glyphosate is bound to the soil through the phosphonic acid moiety (17).

The strong adsorption of glyphosate to soil reduces its mobility through leaching and surface washout. The mobility of glyphosate in Ray, Norfolk, and Drummer soils (see above) has been examined by Rueppel, et al. (10). Soil thin-layer plates were spotted with ^{14}C-glyphosate and developed twice with water; the distribution of ^{14}C activity relative to the origin was determined by beta camera analysis after each development. The parent compound was so strongly adsorbed by all three soils that 97-100 percent of the ^{14}C activity had an R_f of less than 0.09. Similarly, 95-99 percent of the starting ^{14}C activity remained at an R_f of less than 0.09 after the second development. In no case was any of the radioactivity of an R_f greater than 0.18. These values correspond to a Class 1 pesticide (immobile) in the Helling and Turner pesticide mobility classification system (18). (Class 1, 0.0-0.9; Class 2, 0.1-0.34; Class 3, 0.35-0.64; Class 4, 0.65-0.80; Class 5, 0.90-1.00.)

Comes, et al. (19) investigated leaching of glyphosate from banks of irrigation canals treated with glyphosate. Neither glyphosate nor its primary soil metabolite, aminomethylphosphonic acid (AMPA, see Section 3.2.2), were detected in the first flow of water through two canals following application of Roundup herbicide at 5.6 kg/ha to ditchbanks when the canals were dry. Soil samples collected the day before canals were filled (about 23 weeks after treatment) contained about 0.35 ppm glyphosate and 0.78 ppm AMPA in the 0 to 10-cm layer. Soil column leaching studies conducted by the Monsanto Company have also indicated limited potential for leaching (16). In these studies, soil columns treated with either glyphosate or its sodium salt were aged for 30 days prior to eluting with 1/2 acre inch of water for 45 days; leaching of parent compound was insignificant.

Rueppel, et al. (10) also evaluated the runoff potential from Ray, Drummer, and Norfolk inclined soil beds at 7.5° using a rate of 1.12 kg/ha applied uniformly to the upper third of the soil surface. The entire soil surface was then subjected to three artificial rainfalls at 1, 3, and 7-day intervals after treatment. Each time, rainfall was continued through collection of two consecutive 50-ml samples of runoff water and sediment. The water was separated from the sediment by centrifugation and the ^{14}C content of each determined. In both the sediment and runoff water, the amount of ^{14}C activity collected was extremely low, ranging from 6.5×10^{-3} down to 1×10^{-4} percent of that applied for the water and 3×10^{-3} to 1×10^{-5} percent for the sediment. These data correspond to a maximum runoff of less than 2×10^{-4} kg/ha. The lack of runoff is not surprising in lieu of the tight binding of glyphosate to soil discussed above.

3.2.2 Degradation

Studies conducted by Sprankle, et al. (17) and Rueppel, et al. (10) have indicated that glyphosate degradation in soil is relatively rapid and takes place microbiologically, and not by chemical action. Rueppel, et al. (10) conducted soil/water "shake flask" experiments to investigate, under aerobic and anaerobic, and sterile and non-sterile conditions, the mechanism and rate of glyphosate degradation and the nature of degradation products. Each shake flask contained 4.5 g (dry weight) of soil, 1 mg of a ^{14}C-glyphosate and 100 ml of distilled water. Three different ^{14}C-glyphosates were used: N-phosphono-^{14}C-methylglycine, N-phosphonomethylglycine-1-^{14}C, and N-phosphonomethylglycine-2-^{14}C. Four agricultural soils studied were Ray silt loam, Drummer silty clay loam, Lintonia sandy loam, and Norfolk sandy loam, with organic matter contents of 1.0, 6.0, 1.1, and 1.0 percent, respectively. The results of these experiments and two other experiments using sucrose-^{14}C and sucrose-^{14}C plus unlabelled glyphosate are presented in Table 1 for Ray silt loam soil. As shown in the table, all 3 carbons of glyphosate were rapidly degraded at comparable rates in the presence of Ray silt loam. In addition, all three ^{14}C-labelled compounds were degraded to nearly the same extent and rate as the natural and general metabolite sucrose. From the three ^{14}C labels, 47-55 percent of glyphosate ^{14}C was given off as $^{14}CO_2$ in 4 weeks, compared to 57.9 percent for sucrose. Experiments using autoclaved soil/water slurries indicated negligible (less than 1 percent) evolution of $^{14}CO_2$ from the three ^{14}C-labelled glyphosates and the control sucrose^{14}C during a 7-day observation period.

Rueppel, et al. (10) also analyzed the supernatants and soils in shake flasks to determine the distribution of ^{14}C labelled compounds between the two phases and to identify metabolites. The metabolite distribution was similar for both the aerobic and anaerobic shake flasks for a given soil. In general, the same metabolites were observed regardless of the soil type. The principal soil metabolite observed from the N-phosphonic-^{14}C-methyl label of glyphosate was aminomethylphosphonic acid (AMPA); as expected, due to the ^{14}C-label position, this metabolite was not observed radioactively from the two glycine-^{14}C labels. The maximum amount of AMPA detected in the supernatant was 15 per-ent of the starting ^{14}C activity. Several other metabolites were also detected chromatographically in some cases. These minor metabolites included N-methylaminomethylphosphonic acid, glycine, N,N-dimethylaminomethylphosphonic acid, hydroxymethylphosphonic acid, and two unknown metabolites; none of these minor metabolites were normally present to an extent greater than 1 percent of the applied radioactivity. No metabolic products containing an intact N-(phosphonomethyl)glycine grouping were detected in these studies.

Analysis of the shake flask soils, carried out by TLC/beta camera analysis of a soil extract obtained by extraction with 0.5 m NH_4OH, indicated that the extractable residue consisted primarily of the parent glyphosate and the major metabolite AMPA. As in the case with the shake flask super-

TABLE 1. $^{14}CO_2$ EVOLUTION FROM SHAKE FLASKS AS A FUNCTION OF TIME AND ^{14}C LABEL FOR RAY SILT LOAM SOIL (10)

^{14}C Label	Type of Metabolism[†]	Percent ^{14}C Released as $^{14}CO_2$ at 30°C at Day Analyzed					Total ^{14}C as $^{14}CO_2$
		3	7	14	21	28	
N-phosphono ^{14}C-methyl[*]	A	13.2	16.7	10.1	4.6	2.2	46.8
	An	6.2	8.2	17.8	3.7	1.4	37.3
Glycine 1-^{14}C[*]	A	28.1	10.1	13.8	1.9	1.4	55.3
	An	12.6	14.8	18.9	4.8	1.3	51.4
Glycine 2-^{14}C[*]	A	19.0	16.2	12.8	4.0	3.3	55.3
	An	3.8	6.8	9.9	5.9	7.1	33.5
Sucrose ^{14}C	A	41.5	5.3	4.9	3.0	2.4	57.9
	An	34.3	10.1	5.3	3.1	2.5	55.3
Sucrose ^{14}C plus Unlabelled glyphosate	A	26.7	13.0	11.7	2.2	2.0	55.6
	An	22.3	9.5	7.4	11.5	10.8	61.5

[*] Labelled N-(phosphonomethyl)glycine.

[†] Aerobic (A); anaerobic (An).

natants, several minor metabolites were also observed, and the same general distribution was observed on both the aerobic and anaerobic soils. Combustion analysis of the soils after extraction with NH_4OH indicated that from 8.5 to 40.3 percent of the applied ^{14}C activity was bound to soil. Although the bound residue material could not be identified, the NH_4OH non-extractable residue was considered to represent the extensively metabolized products of glyphosate and AMPA.

Shake flask studies of ^{14}C-labelled AMPA indicated that this major metabolite of glyphosate is also highly biodegradable. Aminomethyl-^{14}C-phosphonic acid shake flask studies with Ray silt loam and Drummer silty clay loam soils gave 34.8 and 16.1 percent, respectively, of the applied ^{14}C as $^{14}CO_2$ in 63 days. The slower degradation of AMPA compared to glyphosate was explained in terms of its possible tighter binding to soil and/or lower permeability through the cell walls of microflora.

Based on shake flask slurry studies and dissipation experiments with moist soil (which confirmed the shake flask results), Rueppel, et al. (10) concluded that glyphosate is clearly a biodegradable compound in the presence of soil microflora and that the rate and extent of metabolism are rapid and complete.

3.3 PERSISTENCE IN WATER

The stability of glyphosate in water has been studied by Monsanto Company in laboratory tests conducted under sterile and non-sterile conditions (25). In these experiments, the sodium salt of glyphosate was incubated in sterile water at pH values of 3.0, 6.0, and 9.0 at 25 and 250 ppm. The solutions were incubated in the dark at 5° and 35°C for 32 days. Samples were taken at 0, 7, 14, 21, and 32 days. In addition, three natural water samples ranging from pH 4 to pH 7.3 were treated with 0.1 ppm and incubated in the dark for 7, 21, 35, and 49 days. Glyphosate was stable in sterile conditions with slow biodegradation occurring in natural water.

The data reported indicate the following half-lives in natural water systems (25): Sphagnum bogs (pH 4.23), 7 weeks; cattail swamp (pH 6.25), 9 weeks; and pond water (pH 7.33), 10 weeks. Monsanto reports that, as with soil, microbial breakdown is the major route of degradation of glyphosate in water. The material is tightly adsorbed to organic and mineral matter within the aquatic system and then degraded. Rates of degradation are slower than in most soils due to the lower numbers of microbes in the aquatic system (21).

4.0 IMPACT ON NON-TARGET ORGANISMS

4.1 PLANTS

In applications in the Northeast for conifer release, some "browning" of conifers have been observed with glyphosates at normal application rates of 1 to 2 quarts per acre; this browning, however, has been temporary, and the conifers (e.g., Jack and red pines) have gradually recovered (8). Monsanto has conducted field studies on the potential for drift when Roundup herbicide is applied by air. Their results show that at wind speeds of 12 mph, damaging drift is not likely to move more than 200 ft outside the target. With rates of 2 quarts or less per acre, Monsanto recommends a buffer zone of 75 ft. For rates above 2 quarts, 125 ft is recommended; and a general restriction of 200 ft around homesteads and recreational areas is recommended (21).

As discussed previously, once the glyphosate enters soils, it is inactivated relatively rapidly via adsorption and microbial degradation. In agricultural applications, use of glyphosate at proposed rates has been shown to have no injurious effects on crops planted immediately after herbicide treatment (15). In sand cultures where glyphosate adsorption is minimal, high dosages of glyphosate have been shown to reduce height and shoot growth in several crops. The effect of 0.57 kg/ha of glyphosate applied in sand culture on the growth of seven crop species is shown in Table 2. Based on the data in Table 2, a wide spectrum of sensitivity to glyphosate can be expected. Of the species tested, flax is the most sensitive; corn, soybean and bean are less sensitive than flax, while barley, oat and cucumber are the least sensitive of all. Data presented by Sprankle, et al. (15) also indicated that the germination of corn, soybean and wheat is unaffected by glyphosate application rates of as high as 4.5 kg/ha. Table 3 shows that the dry weight of young wheat plants was not affected by glyphosate applied to the soil at rates of 4.48 and 11.2 kg/ha (15). (The highest recommended application rate for forest uses is about 5 kg/ha of glyphosate.)

TABLE 2. THE EFFECT OF 0.56 kg/ha OF GLYPHOSATE* APPLIED IN SAND CULTURE ON THE GROWTH OF SEVERAL CROP SPECIES (15)

Species	Percent of Control†‡		
	Plant Ht.	Shoot Fresh Wt.	Shoot Dry Wt.
Flax	14 a	21 a	20 a
Corn	35 b	48 bc	45 b
Soybean	36 b	42 ab	33 ab
Wheat	56 c	55 bc	52 b
Barley	68 d	72 cd	71 c
Oats	82 e	116 d	100 c
Cucumber	75 de	69 cd	86 c

*Mono(dimethylamine) salt of glyphosate.

†Means within a column with common letters are not significantly different at the 5 percent level by Duncan's multiple range test.

‡The control is the treatment where 0.8 percent surfactant was applied to the sand.

TABLE 3. THE EFFECT OF GLYPHOSATE ON THE DRY WEIGHT PER PLANT OF 16-DAY-OLD WHEAT PLANTS FOLLOWING INCORPORATION INTO HILLSDALE SANDY CLAY LOAM AT SEVERAL pH LEVELS (15)

pH	Glyphosate* (kg/ha)			
	0 (mg)†	4.48 (mg)†	11.2 (mg)†	56.0 (mg)†
4.6	20 ab	15 a	19 ab	16 ab
5.1	40 de	39 de	42 de	37 cd
5.6	44 c	43 c	44 c	32 c
6.1	43 de	43 de	43 de	21 b
6.7	40 de	40 de	40 de	18 ab

*Isopropylamine salt of glyphosate.

†Means with common letters are not significantly different at the 5 percent level by Duncan's multiple range test.

Yates, Akesson, and Bayer (27) looked at the effects of spray drift on wheat and grape plants. Exposure to plants was measured by measuring the amount of glyphosate deposited on Mylar plates. Previous studies found an excellent correlation between deposit on Mylar plates and residues on alfalfa. The tests found a rather wide band of injury levels as related to deposit levels. For example, some low levels of injury occurred at levels as low as 0.1 to 1 g/ha while some values as high as 10 g/ha produced no injury. The authors state that the data from this study can be used to indicate rough guidelines for the most sensitive conditions. For example, they found that a 10 g/ha exposure on mylar sheets could result in a 70 percent injury on wheat at the 4-leaf stage of growth. For grape plants, the band of injury levels were somewhat lower (i.e., less injury) but similar to the response of wheat plants. The data also showed that the grape plants tended to grow out of the symptoms in time.

4.2 FAUNAL IMPACTS

Data on the toxicity and limited data on the effects of Roundup on habitat suitability indicate that Roundup can be used in the forest without resulting in toxic effects to forest fauna.

Folmar, et al. (9) conducted several experiments on the effects of glyphosate and glyphosate formulations on aquatic ecosystems. Among the tests conducted were acute toxicity assays for Roundup on several aquatic invertebrates and fishes. As shown in Table 4, the 96-hr LC_{50} values varied from 2.3 mg/L for fathead minnows to 43 mg/L for mature scuds. In Table 5, it can be seen that under "worse case" conditions, the LC_{50} for rainbow trout can be as low as 1.4 mg/L. The toxicities determined for the other organisms were nearer the values for fathead minnows than for the more resistant scuds.

Tests comparing the toxicities of the technical grade glyphosate, Roundup and the surfactant used in the Roundup formulation have indicated that the surfactant, and not the glyphosate, is the primary toxic agent in Roundup (9) (see Tables 5 and 6). As shown in Table 4, the 24-hr LC_{50} for rainbow trout is 140 mg/l for glyphosate and only 2.1 mg/l for the surfactant. The data in Table 5 also illustrate the effect of pH on aquatic toxicity of Roundup and its glyphosate and surfactant components. Except for the glyphosate which appears to be more toxic at a pH of 6.5 than at a pH of 9.5,

TABLE 4. TOXICITY OF ROUNDUP TO AQUATIC INVERTEBRATES AND FISH (9)

Organisms	Temp. (°C)	LC_{50} or EC_{50}* (mg/L) and 95% Confidence Limits		
		24 h	48 h	96 h
Daphnids	22		3.0 (2.6-3.4)	
Scuds	12	100	62 (40-98)	43 (28-66)
Midge larvae	22		18 (9.4-32)	
Rainbow trout	12	8.3 (7.0-9.9)		8.3 (7.0-9.9)
Fathead minnows	22	2.4 (2.0-2.9)		2.3 (1.9-2.8)
Channel catfish	22	13 (11-16)		13 (11-16)
Bluegills	22	6.4 (4.8-8.6)		5.0 (3.8-6.6)

*Daphnid and midge toxicities expressed as 48-h EC_{50} (concentration immobilizing 50 percent of the test organisms).

TABLE 5. TOXICITY OF TECHNICAL GLYPHOSATE AND THE ROUNDUP SURFACTANT TO MIDGE LARVAE AND FOUR SPECIES OF FISH (9)

Chemical and Organism	Temp. (°C)	LC_{50} or EC_{50}* (mg/L) and 95% Confidence Limits		
		24 h	48 h	96 h
GLYPHOSATE				
Midge larvae	22		55 (31-97)	
Rainbow trout	12	140 (120-170)		140 (120-170)
Fathead minnows	22	97 (79-120)		97 (79-120)
Channel catfish	22	120 (110-160)		130 (110-160)
Bluegills	22	150 (120-190)		140 (110-160)
SURFACTANT				
Midge larvae	22		13 (7.1-24)	
Rainbow trout	12	2.1 (1.6-2.7)		2.0 (1.5-2.7)
Fathead minnows	22	1.4 (1.2-1.7)		1.0 (1.2-1.7)
Channel catfish	22	18 (8.5-38)		13 (10-17)
Bluegills	22	3.0 (2.5-3.7)		3.0 (2.5-3.7)

*Midge toxicity expressed as 48-hr EC_{50} (concentration immobilizing 50 percent of the test organisms).

TABLE 6. EFFECTS OF pH ON TOXICITY OF ROUNDUP, GLYPHOSATE, AND THE SURFACTANT TO RAINBOW TROUT AND BLUEGILLS (9)

Chemicals, Organism, and pH	LC_{50} (mg/L) and 95% Confidence Limits	
	24 h	96 h
ROUNDUP		
Rainbow trout		
6.5	14 (12-17)	7.6 (6.4-9.1)
7.5	2.4 (2.0-2.9)	1.6 (1.2-2.2)
8.5	2.4 (2.0-2.9)	1.4 (1.2-1.7)
9.5	2.4 (2.0-2.9)	1.4 (1.2-1.7)
Bluegills		
6.5	7.6 (6.4-9.1)	4.2 (3.5-5.0)
7.5	4.0 (3.2-5.0)	2.4 (2.0-2.9)
8.5	3.9 (3.1-4.9)	2.4 (2.0-2.9)
9.5	2.4 (2.0-2.9)	1.8 (1.3-2.5)
GLYPHOSATE		
Rainbow trout		
6.5	240 (200-290)	140 (120-170)
9.5	240 (200-290)	240 (200-290)
Bluegills		
6.5	240 (200-290)	140 (120-170)
9.5	230 (190-280)	220 (170-280)
SURFACTANT		
Rainbow trout		
6.5	7.4 (6.2-8.9)	7.4 (6.1-9.0)
9.5	1.4 (1.2-1.7)	0.65 (0.54-0.78)
Bluegills		
6.5	4.2 (3.1-5.7)	1.3 (1.1-1.6)
9.5	3.0 (2.2-4.1)	1.0 (0.72-1.4)

all three chemicals were less toxic to the species tested at the lower pH value of 6.5.

Folmar, et al. (9) also investigated the effects of temperature on the toxicity of Roundup to two species of fish. The results, shown in Table 7, indicate that Roundup is about twice as toxic to rainbow trout at 17°C than it is at 7°C, and that it is more toxic to bluegills at 27°C than at 17°C.

TABLE 7. EFFECTS OF TEMPERATURE ON THE TOXICITY OF ROUNDUP TO TWO SPECIES OF FISH (9)

Organism and Temp. (°C)	LC_{50} (mg/L) and 95% Confidence Limits 24 h	 96 h
Rainbow trout		
7°	14 (11-17)	14 (11-16)
12°	14 (11-17)	7.5 (6.3-9.0)
17°	7.5 (6.3-9.0)	7.4 (6.2-8.9)
Bluegills		
17°	9.6 (7.9-12.0)	7.5 (6.3-9.0)
22°	6.4 (4.8-8.6)	5.0 (3.8-6.6)
27°	4.3 (3.4-5.4)	4.0 (3.2-5.0)

Folmar, et al. (9) also conducted experiments on mayfly avoidance of Roundup and rainbow trout avoidance of the isopropylamine salt of glyphosate. In these tests, rainbow trout did not avoid concentrations of the isopropylamine salt up to 10 mg/L; mayfly nymphs avoided Roundup at concentrations of 10 mg/L but not at 1.0 mg/L.

Folmar, et al. (9) exposed various early life stages of rainbow trout and channel catfish to Roundup. The results of their tests indicated that, for both species, the egg stage was the least sensitive and that the toxicity of Roundup increased in the sac fry and early swim-up stages, but decreased in the fingerling stage as the fish grew larger. Significant reductions in the hatch of trout eggs was observed at 10 mg/L whereas no significant difference was observed at 5.0 mg/L. A significant reduction in the survival of sac-fry was seen at 5.0 mg/L but not at 2.0 mg/L. These data indicate that applications of Roundup could have adverse effects if applied during seasons when young fish are present in the receiving waters (9).

Although many studies have been conducted, very limited data are publicly available on the toxicity of glyphosate to animals (wildlife and beneficial insects). Feeding studies with mallard duck and quail have indicated an LC_{50} of greater than 4600 ppm of glyphosate (in food) (20). Experiments with bees have indicated an LD_{50} of greater than 100 μg per bee (20). The oral rat LD_{50} for glyphosate is 4320 mg/kg (22).

4.3 BIOACCUMULATION

The limited data available indicate that glyphosate has little to no potential to bioaccumulate when used in forest systems. Trout, bluegills, and bass exposed to 10-12 ppm of Roundup for 14 days contained only 0.1 ppm of glyphosate (20). Upon being placed in clear water, the glyphosate in the "contaminated" fish was depleted (20). The octanol/water partition coefficient for glyphosate is reported to be 0.0017 at 20 ppm and 0.0006 at 100 ppm, indicating virtually no tendency to bioconcentrate in living cells (26).

Folmar, et al. (9) exposed rainbow trout for 12 hours to 0.02, 0.2, and 2.0 mg/L of either the isopropylamine salt of glyphosate or Roundup as a simulation of actual field exposures. No residues of glyphosate or the primary metabolite, AMPA, were detected in either the fillets or eggs of fish exposed to the isopropylamine salt. However, in fish exposed to 2.0 mg/L of Roundup, the fillets contained 80 µg/kg of glyphosate and the eggs contained 60 µg/kg. Midge larvae, from both drift and substrate samples, were collected for 7 days after exposure to Roundup in artificial stream studies. No glyphosate residues were detected in the midge larvae (9).

In another study, rabbits were administered a single oral dose of ^{14}C-glyphosate. Five days after treatment, more than 80 percent of ^{14}C were found in the feces, 7 to 11 percent in urine, less than 1 percent in expired $^{14}CO_2$ and most of the unrecovered ^{14}C was found in the colon (16).

4.4 MICROORGANISMS

Rueppel, et al. (10) investigated the effect of glyphosate on soil microorganisms by measuring the rate of sucrose degradation in treated and untreated soil and by conducting plate counts of treated and untreated soil under aerobic and anaerobic conditions, the rate of degradation of ^{14}C sucrose to $^{14}CO_2$ was similar in both glyphosate-treated and glyphosate-untreated soils. Plate counts appeared to indicate that glyphosate had no adverse effect on the total microflora population. Treatment of Norfolk sandy loam caused a large increase (from 3.8×10^{-5} to 62.0×10^{-5}) in the total number of microorganisms per gram of soil. These findings are generally consistent with those of Quilty and Geoghegan (23) who found glyphosate to have minimal effect on microflora in peat.

Application of glyphosate to three soils - Drummer silty clay loam, Lintonia sandy loam, and Ray silt loam - at 5 and 25 ppm (1 and 5 times normal dose) showed no apparent significant effects on nitrogen fixation or nitrification by microbes (16). Treatment of the three soils mentioned above with 5 and 25 ppm of glyphosate resulted in no apparent effect on cellulose degradation, starch degradation, protein degradation, or leaf litter degradation (16).

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Common Name: Hexazinone

Chemical Name: 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione

Major Trade Names: Velpar® Gridball® Brush Killer; Velpar® Weed Killer; Velpar® L Weed Killer

Major Applications in Forestry: Used primarily in the Southeast and Southwest for site preparation and pine release, and the Northeast to a lesser extent to control undesirable hardwoods in forest situations.

SUMMARY

Velpar® Gridball® Brush Killer is a relatively new herbicide which is being evaluated in large-scale commercial applications in the Southeast, Southwest, Northeast and upper Midwest as a possible substitute for 2,4,5-T for site preparation and conifer release. Because of its relative newness, field trials of "Velpar" to date have primarily emphasized evaluation of efficacy with environmental fate and impact studies in progress. The data which are available on soil residues, degradation, and impacts on non-target organisms are primarily those generated in laboratory, greenhouse, field, and forest studies by the manufacturer or investigators in connection with the registration of various "Velpar" formulations.

Root uptake is the principal mechanism for the absorption of hexazinone by plants from soils treated with "Velpar" "Gridball" pellets. Hexazinone is translocated to the foliage where it blocks the photosynthesis process. In addition to plant uptake, hexazinone is dissipated in soil via photodegradation, biodegradation, and leaching. Laboratory tests in which soil films were subjected to artificial sunlight yielded a photodegradation half-life of 37 days for hexazinone. Greenhouse and field soil degradation tests using ^{14}C-labelled hexazinone have indicated that hexazinone degrades in soil biologically both under aerobic and anaerobic conditions. Depending on field conditions, half-life of hexazinone in soil may be as short as one month or in excess of six months. The half-life appears to be independent of the application rate. Using thin layer chromatography-liquid scintillation counting, several triazine compounds have been identified as hexazinone degradation products. Laboratory and field leaching tests have indicated that hexazinone and some of its degradation products would be washed into the soil with the rainwater. Photodegradation and biological decomposition are the major factors in reducing hexazinone concentration in natural waters.

In applications of "Velpar" "Gridball" for conifer release, some conifer mortality may occur from 0-15 percent, but is dependent on species, rate, soil type, and other factors. Aquatic toxicity data indicate that "Velpar" is only slightly toxic to Daphnia and fish. The product also does not bioaccumulate in fish. Toxicity tests have indicated that "Velpar" is of low toxicity to birds, wildlife, fish, and mammals.

1.0 INTRODUCTION

With the suspension of forestry uses of 2,4,5-T, considerable attention has been focused, particularly in the South, on developing suitable chemical substitutes for 2,4,5-T. DuPont's "Velpar" "Gridball" Brush Killer, which is being evaluated in large-scale commercial trials, appears to hold some promise as a partial replacement for 2,4,5-T. It has been found effective for control of brush at least two inches in diameter at breast height on coarse to medium textured soils when applied as spring treatment. Rainfall is required to dissolve the pellets and move the active ingredient into the root zone of the species to be controlled. Estimates place the total acreage treated in the South at about 20 thousand acres per year, mainly for site preparation (1) and conifer release. Another estimate, based on an industry survey, indicates the following usage of hexazinone in the Southeast for 1979 (2):

Treatment	Hexazinone Formulations	Acres Treated	Lb Used	Method of Application
Site preparation - woody vegetation	"Gridball"	160	1,900	Ground and aerial
Pine release - woody vegetation	"Gridball"	375	5,000	Ground and aerial
Pine release - herbaceous	Soluble powder	6,006	6,006	Ground
Site preparation - kudzu	Soluble powder	5	15	Ground

"Velpar" "Gridball" is currently registered for forestry use in the U.S. east of the Rocky Mountains. It has been tested in the Pacific Northwest, the Southeast, Southwest, upper Midwest, Northeast, and Canada (3). Excellent results have been obtained in tests in Michigan and the Northeast (and in full scale trials in the Southeast and Southwest); results have not been as promising for the Northwest (3). Some difficulties have also been encountered in preliminary tests in the colder climates of Maine and Canada; these, however, are being investigated and the manufacturer feels that "Velpar" "Gridball" may also prove effective in the cold climates.

"Velpar" "Gridball" Brush Killer is recommended for forestry site preparation and conifer release where loblolly, long leaf, short leaf, slash and Virginia pines are grown. It is effective for the control of many woody plants including black cherry, hawthorn, oaks (such as blackjack, bluejack, post, southern red, turkey, water, willow, and white oak), sweetgum, wild plum, and winged elm. Recommended rates for site preparation usually provide control of hard-to-kill species, including flowering dogwood, hickory, persimmon, red cedar, red maple, and sourwood.

"Velpar" "Gridball" pellets are applied by hand or with appropriate aerial equipment such as the modified Simplex Airblown Seeder. Simplex Manufacturing Co. (Portland, Oregon) has developed an applicator device for helicopters for aerial application of "Gridball" pellets. In trials in Oregon and Alabama, the modified seeder was demonstrated to be capable of effectively and uniformly distributing the 1-inch long "Gridball" pellets (4). For hand application, the spacing between the pellets determines the rate of application. For example, to apply 5 lb per acre, pellets must be spaced approximately 8 1/2 feet apart in each direction on the soil surface; for 10 lb per acre, 6 feet apart, etc. The degree of brush control and duration of the effect vary with the amount of product applied, soil type, rainfall, and timing of application. The chemical is applied before or during the period of active brush growth and when rainfall can be expected for soil activation. Reflecting differences in soil characteristics, the recommended label application rates vary somewhat for different states. The recommended label application rates for various soil textures in Alabama are as follows (5,6):

	Pounds Product/Acre		
Soil Texture	Pine Release*	Site Preparation	Species Controlled or Suppressed
Sand	5-6	7 1/2-10	All species listed above
Loamy sand, sandy loam	7-8	10-15	"
Sandy clay loam, silt loam, loam	10	15-20	"
Silty clay loam, clay loam	10	15-20	"

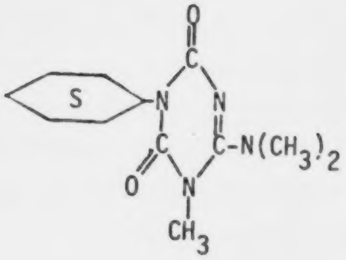
*Pine release rates will not control hard-to-kill species.

According to the label, rates higher than those shown above can cause injury to pines. Based on field results, however, for some "heavy" soils in Alabama, application rates of 30 lb/acre or higher would be required for effective site preparation (1). The level of residue in soil and its potential impact on pine seedlings planted subsequently, however, are not currently known for these very high application rates (1). Data from field applications also indicate variable results in release applications; while at some sites pine mortality has been at acceptable levels, at certain sites a pine mortality of as high as 38 percent was caused by poor distribution of pellets on stressed or sensitive species of pines (6). "Velpar" "Gridball" should not be used on poorly drained sites, on sites dominated by small stemmed brush (<2" DBH) nor on pines which are suffering from loss of vigor caused by insects, diseases, drought, winter injury or other stresses, as severe injury may result (6).

"Velpar" "Gridball" pellets are available as 10 percent or 20 percent active ingredient (7) hexazinone (also referred to as DPX 3674). Another "Velpar" formulation, "Velpar" Weed Killer (also referred to as "Velpar" 90) is a water soluble formulation containing 90 percent active ingredient and 10 percent inerts, and has been used as a foliar spray for control of certain weeds in Christmas tree plantations and reforestation areas and for the control of undesirable woody plant species in non-cropland areas such as railroad, highway, utility and pipeline rights-of-way, petroleum tank farm storage areas and drainage ditchbanks. Other "Velpar" formulations are "Velpar" L (a water dispersible liquid containing 2 lbs hexazinone) with registrations similar to "Velpar" Powder (6). "Velpar" K products (wettable powders containing various combinations of hexazinone plus diuron) are registered for uses outside the U.S. (6,8). E. I. DuPont de Nemours & Co., Inc. (Wilmington, Delaware) is the sole producer of "Velpar" formulations. The company indicates that it has sufficient production capacity to meet the current demand (9). The suggested consumer price for "Velpar" "Gridball" is $3.30 per lb; commercial applicators reportedly charge between $4.00 and $8.50 per acre to apply "Velpar" "Gridball" (9).

2.0 PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE ACTIVE INGREDIENT

3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione (or hexazinone) is the active ingredient of "Velpar" formulations.



Hexazinone

Hexazinone is a white crystalline solid with a specific gravity of 1.25. It has a melting point of 115°-117°C and a vapor pressure 2×10^{-7} mm Hg at 25°C (extrapolated from a vapor pressure of 6.4×10^{-5} mm Hg at 86°C) (8). It is soluble in water to the extent of 3.3 g/100 g at 25°C. Solubility in other solvents are as follows (8):

Solvent	Solubility, g/100 g at 25°C
Chloroform	388
Methanol	265
Benzene	94
Dimethylformamide	83.6
Acetone	79.2
Toluene	38.6
Hexane	0.3

The following data have been reported on the stability and photodecomposition of hexazinone solutions (6,10). Hexazinone slowly degrades in distilled water (under "artificial sunlight" about 15 percent in 8 weeks). The rate of photodegradation is about three times faster when small amounts of inorganic salts are present and about seven times faster in natural river water or in distilled water when a photoinitiator is present. In buffered aqueous solutions in the dark at 5 ppm and 5,990 ppm (representing dilute and spray tank concentrations), the compound is stable (less than 1 percent decomposition) for at least 5 to 8 weeks at pH 5, 7, and 9 and temperatures of 15°C, 35°C, and 37°C (see Section 3.3).

3.0 ENVIRONMENTAL FATE

Since "Velpar" is a new herbicide, most of the interest in this chemical to date has been in connection with the evaluation of its efficacy and the optimum conditions to improve effectiveness. Accordingly, field trials of

"Velpar" use in forestry have not included an evaluation of the environmental fate of "Velpar", until recently. In general, the data which are available now on soil residues, degradation in water and potential impacts on non-target organisms are largely those generated in laboratory and greenhouse studies by the manufacturer in connection with the registration of various "Velpar" formulations. A forest ecosystem study is now in progress to better answer the above questions related to forestry (6).

3.1 UPTAKE AND METABOLISM BY PLANTS

When "Velpar" is used in "Gridball" formulation, the rainfall causes breakdown of the pellets, thereby releasing the hexazinone. The hexazinone is moved downward in soil in concentrated columns and is absorbed from the soil solution by the tree roots and is translocated upward in the conductive tissue to the foliage where it blocks the photosynthetic process and slowly causes the susceptible woody tissue to die. When applied as a foliar spray, the root absorption is supplemented by some direct absorption via foliage. The first visible symptoms of "Velpar" "Gridball" treatment effects are a yellowing and browning of the leaves followed by defoliation. Some trees will defoliate and refoliate in the first growing season after application. Other trees may follow this pattern and, also, put out new leaves in the second growing season after application; they will, however, gradually defoliate. The defoliated trees will ultimately die.

Metabolism studies have been conducted on sugarcane and alfalfa. Dormant alfalfa in the field, treated with 1 lb a.i./acre ^{14}C-labelled hexazinone, contained 0.5, 0.5, and 0.1 ppm total ^{14}C-residues when harvested at two, three, and six months, respectively. At least 70 percent of the total ^{14}C-residues in the two-month cutting was identified as natural products; about 15 percent of the total ^{14}C-residues consisted of free and conjugated hexazinone metabolites (12 percent) and intact hexazinone (3 percent), for a total of 84.9 percent identified radioactivity (11).

When sugarcane in the greenhouse was treated with 1.0 and 0.5 kg a.i./ha ^{14}C-labelled hexazinone, total radioactive residues at harvest were 0.07 to 0.08 ppm and 0.05 ppm, respectively. These residues consisted mainly of 42 percent metabolite E (see Figure 1), 32 percent metabolite C, 20 percent metabolite A, and less than 1 percent hexazinone (12).

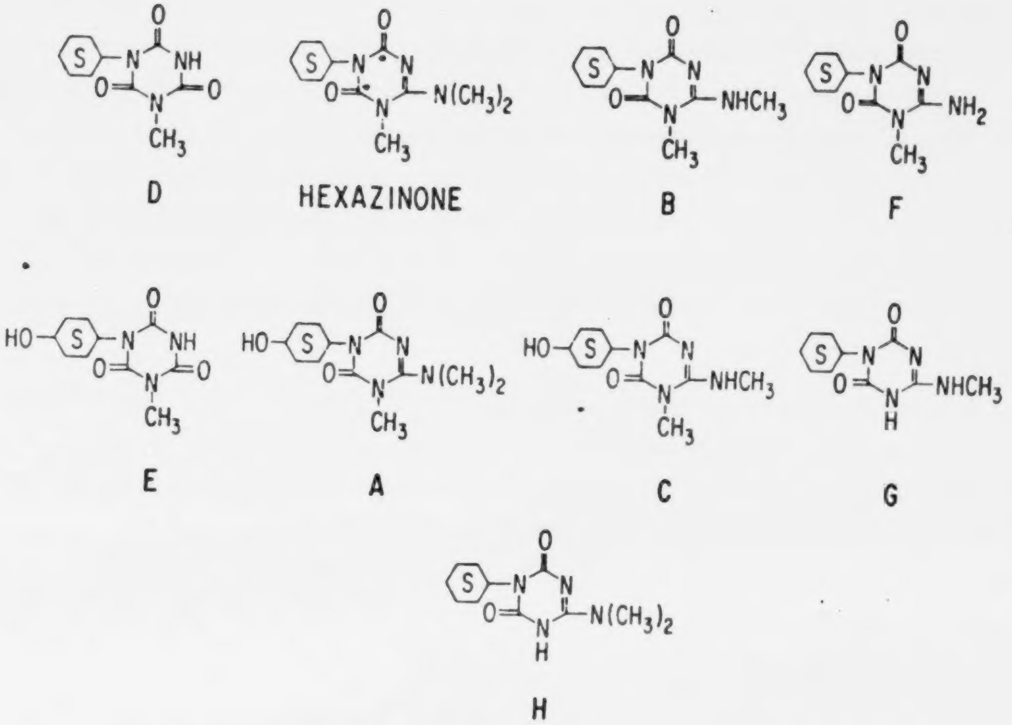


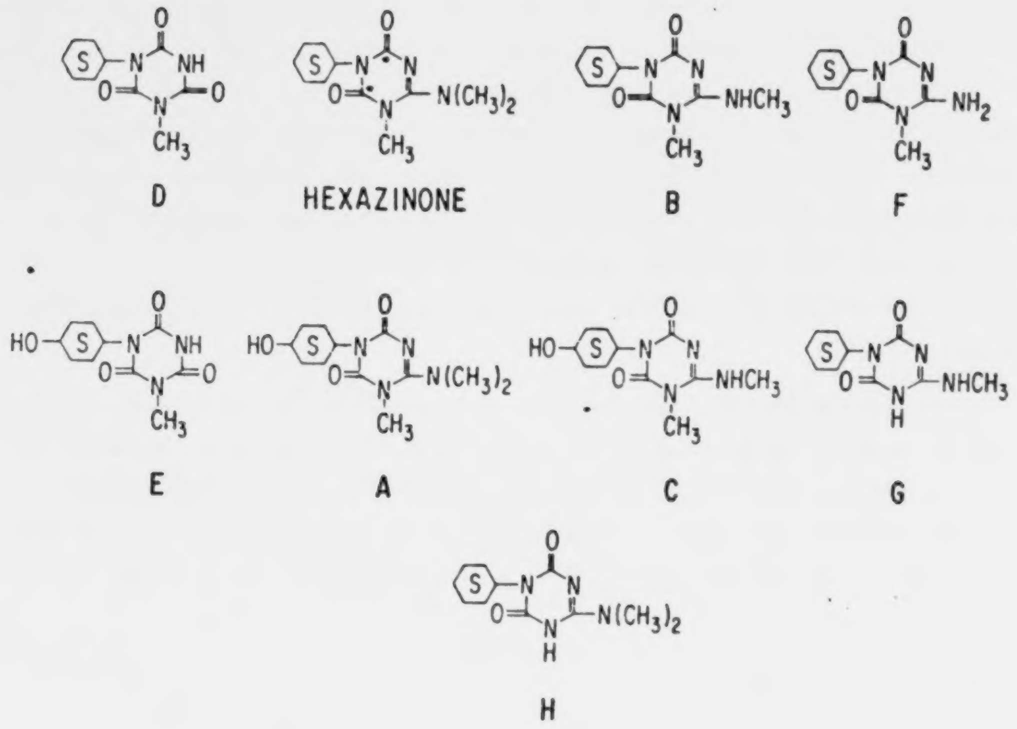
Figure 1. Structures of Degradation Products of Hexazinone (10,14)

3.2 FATE IN SOIL

The major routes for the dissipation of hexazinone in soil are photodegradation, biodegradation, and leaching. Volatilization is not considered to be a significant contributor to hexazinone losses from the soil because of the very low vapor pressure of hexazinone (see Section 2.0).

3.2.1 Photodegradation

Hexazinone on the soil surface is subject to photodegradation under the action of sunlight. In a study by DuPont (13), Flanagan silt loam (organic matter 4 percent) was treated with 10 ppm of ^{14}C-parent compound, slurried and placed in petri dishes. Soil film thickness was about 500 microns. The photosource was artificial sunlight at six inches from the soil film. Exposure continued for six weeks. Samples were extracted with 90:10 acetone: water, and analyzed by TLC-LSC (thin layer chromatography-liquid scintillation counting). Non-extractable ^{14}C was analyzed by total combustion-LSC



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Photodegradation of hexazinone on soil surfaces has also been demonstrated in studies where hexazinone was applied to silica gel plates as a narrow streak and exposed to artificial light (13). After three weeks of exposure, the percent activity found at each R_f value was R_f 0.00, 13 percent; R_f 0.13, 22 percent; R_f 0.27, 8 percent; R_f 0.40, 41 percent; R_f 0.8, 4 percent; and R_f 0.9, 12 percent.

3.2.2 Biodegradation

Greenhouse soil metabolism tests conducted by DuPont (14) using ^{14}C-labelled hexazinone have indicated that hexazinone is degraded by the action of soil microorganisms both under aerobic and anaerobic conditions, although the rate of degradation is somewhat slower under anaerobic conditions. Two soil types (Fallsington sandy loam and Flanagan silt loam, 1.4 percent and 4.02 percent organic matter content, respectively) were fortified with 4 ppm hexazinone. Moisture content was maintained and samples were taken periodically. Water/acetone extracts of the samples were analyzed by a TLC-LSC procedure. The results indicated that under aerobic conditions the time required for 50 percent degradation was less than 4 months in both soil types. The half-life for total radioactive residues was greater than 6 months; 65 percent and 68 percent of the applied ^{14}C was present in Fallsington sandy loam and Flanagan silt loam soils, respectively, after a 6-month greenhouse exposure. The major metabolites in the greenhouse soils were compounds A, B, and D (Figure 1) in contrast to the field studies (see below) where compound C was the major metabolite. No degradation of hexazinone or loss of radioactivity occurred when Fallsington sandy loam and Flanagan silt loam, treated with 4 ppm (^{14}C)hexazinone, were maintained under anaerobic conditions for a 60-day period.

Laboratory studies in biometer flasks with the two soil types treated with (^{14}C)-hexazinone (4 and 20 ppm) indicated that hexazinone is degraded by microbial action. The results (14) show that after an initial lag period of 10-20 days, the rate of $^{14}CO_2$ evolution increased rapidly. After 80 days, 45-75 percent of the applied radioactivity had been evolved as $^{14}CO_2$. These data suggest that the triazine ring is totally degraded to liberate $^{14}CO_2$. No $^{14}CO_2$ was detected in the treated sterile Fallsington sandy loam, and only trace amounts were found from the treated sterile Flanagan silt loam.

Studies to determine the fate of ^{14}C hexazinone in soil under actual field conditions have been conducted on test sites at Newark, DE (Keyport silt loam); Rochelle, IL (Flanagan silt loam); and Scott, MS (Dundee silt loam) (14). At each location, cylinders were driven into undisturbed soil and the soil inside each cylinder was treated with ^{14}C hexazinone at the rate corresponding to 3.7 kg/ha. Cylinders from each location were dug up at regular intervals and depth increments analyzed. The results indicated the following half-life values for intact ^{14}C hexazinone: 1 month in Delaware, 2 months in Illinois, and 6 months in Mississippi. The time for 50 percent loss of total radioactive residues was: 3-4 months in Delaware, 6-7 months in Illinois, and 10-12 months is Mississippi. The major routes of degradation of hexazinone in soil were determined to involve both demethylation and hydroxylation of the 4 position of the cyclohexyl ring. The major metabolite at each location was metabolite C (Figure 1). Other soil metabolites present in significant amounts at each location were metabolites A, B, and G. The soil metabolites have been shown to be degradation products of hexazinone in the rat and in water.

In a separate study (13), the above mentioned field experiments with the Keyport silt loam were extended to include an evaluation of the effect of application rate on persistence of hexazinone in soil. Four application rates (1.8, 4.0, 9.2, and 20 lb a.i./acre) were evaluated. At the highest application rate of 20 lb a.i./acre incorporated (15 ppm in soil, calculated), about 15 percent of hexazinone remained in soil after 6 months as combined hexazinone and metabolites A and B. Some leaching of the parent compound down to a depth of 12-18 in. was also observed. When surface applied at a rate of 9.2 lb a.i./acre (6.9 ppm, calculated), the concentration of the parent compound after 8 months was 0.12 ppm. Test results indicated that the half-life of hexazinone was apparently independent of the application rate for the soil type and dosages tested.

In a more recent field study (15) conducted by the U.S. Forest Service Southern Forest Experiment Station, "Velpar" 90W, at 2 and 4 kg/ha, was applied by a tractor-mounted boom sprayer to experimental plots of Pacolet clay and Uchee loamy sand in Alabama. A composite soil sample consisting of 30 cores (1.9 cm in diameter) was taken from each herbicide-treated plot. Sampling dates were 0, 4, 8, 16, 24, 36, and 49 weeks after treatment. Each soil core was divided into 3 increments: 0-8 cm, 8-16 cm, and 16-24 cm. All soil samples were air dried, screened through a 2 mm sieve, stored in a glass jar, and refrigerated until analysis. Both oat (Avena fatua var. Florida 501) shoot dry weight bioassay and gas-liquid chromatographic analysis (GC) were used to determine the concentrations of hexazinone in the soils. For both oat bioassay and GC analysis, the half-life of hexazinone was about 4-6 weeks in Pacolet clay. In Uchee loamy sand, the half-life of hexazinone was less than 4 weeks according to both methods. Hexazinone metabolites A and B were found in both Pacolet clay and Uchee loamy sand soils. Metabolite C was found in the Pacolet clay soil only.

In a companion field study by the Southern Forest Experiment Station where the "Gridball" was used instead of the "90W" (15), a half-life of approximately 14 weeks was obtained on a deep (100") sandy soils. The hexazinone was metabolized and metabolites A and B were detected at low levels.

3.2.3 Leaching and Runoff

As part of the field soil degradation studies mentioned above, DuPont also evaluated the potential for leaching of hexazinone from the soils tested. The results indicated that hexazinone and at least some of its degradation products are washed into the soil with the rainwater. The distributions of ^{14}C as a function of the soil depth and total rainfall were as shown in Tables 1 and 2 for Keyport silt loam and Flanagan silt loam, respectively.

DuPont (6,13) has also reported on laboratory column leaching studies with Flanagan silt loam (organic content 4 percent, pH 5.0, and cation exchange capacity 23.4 me/100 g) and Fallsington sandy loam (organic content

TABLE 1. LEACHING OF HEXAZINONE IN KEYPORT SILT LOAM[*] (13)

Soil Depth (in.)	% of Applied ^{14}C			
0 - 1	99.4	26.8	17.2	11.6
1 - 3	<0.1	24.3	17.1	16.8
3 - 5	<0.1	7.4	11.7	18.2
5 - 8	<0.1	5.0	4.2	9.6
8 - 12	<0.1	2.7	3.8	6.2
	99.4	66.2	54.0	62.4
Total rainfall (inches)	0.00	8.43	12.29	13.79
Exposure time (month)	0	1	2	3

[*] Composition and characteristics: sand 21 percent, silt 62 percent, clay 17 percent, organic matter 2.75 percent, nitrogen 0.097 percent, cation exchange capacity 8.2 me/100 g.

TABLE 2. LEACHING OF HEXAZINONE IN FLANAGAN SILT[*] LOAM (13)

Soil Depth (in.)	% of Applied ^{14}C		
0 - 1	99.0	103.5	22.4
1 - 3	<0.1	0.2	38.6
3 - 5	<0.1	<0.1	17.9
5 - 8	<0.1	<0.1	2.5
8 - 12	<0.1	<0.1	0.5
12 - 15	<0.1	<0.1	<0.1
	99.1	103.7	81.9
Total rainfall (inches)	0.00	0.25	7.04
Exposure time (months)	0	0.5	1.50

[*] Composition and characteristics: sand 5 percent, silt 64 percent, clay 31 percent. organic matter 4.02 percent, nitrogen 0.282 percent, pH 5.0, and cation exchange capacity 23.4 me/100 g.

1.4 percent, pH 5.6, and cation exchange capacity 4.8 me/100 g). Freshly applied and "aged" (30 days) ^{14}C-hexazinone was applied at a 4 lb a.i./acre rate. Water was percolated through the prewetted columns at the rate of 0.2 in/hr until a total of 20 inches was collected. 0.2-in increments were collected for analysis. A sodium chloride-^{36}Cl breakthru volume test was also run.

With the sandy loam 87 percent and 64 percent of the applied radioactivity percolated through the columns for fresh and "aged" soils, respectively, in 20 inches of water. Highest concentrations occurred at 5 inches for sodium chloride, 8 inches for freshly treated soil and 10 inches for aged soil.

With silt loam soil 27 percent and 0.1 percent of applied radioactivity eluted with 20 inches of water for fresh and "aged" samples, respectively. Highest concentrations occurred at 18 inches for the unaged sample and 7 inches for sodium chloride.

Two-inch increments of the "aged" samples were removed from the columns and analyzed. The radioactivity remaining in the column was evenly distributed over the length.

The soil column leaching tests thus indicated that hexazinone is leached in the soils. Leaching rates are much lower for "aged" samples, indicating the formation of less water soluble or more highly adsorbed degradation products.

Rhodes (14) reported on soil TLC mobility tests using the techniques of Helling and Turner. R_f values were 0.85 for Fallsington sandy loam, 0.68 for Flanagan silt loam, 0.75 for Keyport silt loam, and 0.90 for Cecil loamy sand. These values correspond to a Class 4 pesticide (very mobile) in the Helling and Turner pesticide mobility classification system (16) (Class 1, 0.0-0.09; Class 2, 0.1-0.34; Class 3, 0.35-0.64; Class 4, 0.65-0.80; Class 5, 0.80-1.00).

Neary, et al. (17) studied the subsurface movement of hexazinone in forest watersheds. Small forest watersheds in the upper Piedmont of Georgia were treated with 16.8 kg/ha of hexazinone pellets for site preparation. Movement of hexazinone and two metabolites in storm runoff was measured using

30 cm H-flumes, equipped with water-level recorders, and Coshocton wheel flow-proportional samplers. Hexazinone concentrations in a sandy loam typic hapludlt were monitored by soil samples collected on the lower, mid-, and upper slopes. A series of 19 storms sampled in the last 8 months of 1979 produced a residue loss in runoff amounting to 0.5 percent of the applied hexazinone (31 percent of the chemical which fell directly into ephemeral channels). In the soil, a downslope, concentrating wave of hexazinone residues was observed in the 0 to 10 cm depth. Concentrations peaked 3 days after the first rainfall at the upper and mid-slope positions, but continued to climb at the slope base for 60 days. Hexazinone residues in the soil fell below detection levels by 90 days after the first storm. During a 17 day period immediately thereafter, two peaks of hexazinone residues were detected in a first order perennial stream below the treated area. Streamflow during this period originated entirely from baseflow as no rainfall occurred. The peak stream concentration was 23 ppb, consisting of equal portions of hexazinone and one metabolite. The subsurface movement of residues produced an additional loss of 0.02 to 0.05 percent of the chemical originally applied to the watersheds.

In connection with the above field study, Mayack, et al. (18) and Neary, et al. (19) reported on hexazinone residue (hexazinone plus metabolites A and B) in solution in a perennial stream 250 m below the watershed. Metabolite B was never detected. For much of the experimental period, hexazinone residue was below 1 ppb analytical detection limit. Detectable concentrations (6 to 44 ppb) consisting of metabolite A and hexazinone occurred during very short periods, primarily during the third and fourth months after herbicide application. Peak residue levels, however, did not show any direct relationship to the magnitude of storm events, nor did periods of elevated concentrations coincide with all storm events.

In a more recent study by the Southern Forestry Experiment Station (1), "Velpar" "Gridball" was placed on deep sandy soil in a recently-burned area (to represent the "worst" case in forestry application). Application was made in 1979 at a rate of one 2 cc "Gridball" pellet (10 percent hexazinone) on a 6' x 6' grid. Soil samples were collected at the time of application and 1 week, 2 weeks, 4 weeks, 2 months, 4 months, 8 months, and 12 months after application; sampling depths were 0-6 inches, 6-18 inches, and 18-30 inches directly under pellets and around the periphery of pellets (circles of 12-, 24-, and 36-inch diameter). Thus, at each sampling time, a total of 90 samples were collected. Preliminary results from analysis of the samples indicated (15) rapid vertical but little lateral hexazinone movement (less than 12 inches laterally in any direction).

3.3 PERSISTENCE IN WATER

Rhodes (10) studied the degradation of hexazinone in aqueous systems. The available data indicate that photodegradation and biological decomposition are the major contributing factors to the reduction of hexazinone concentration in natural waters; hydrolysis does not appear to contribute to hexazinone dissipation.

Hydrolysis studies consisted of tests run on the following solutions of ^{14}C-labelled hexazinone: (a) 5990 ppm (5 lb/100 gal) in 0.05 M pH 5.7 and 9 aqueous buffers at 15°C; (b) 5 ppm in 0.05 M pH 5.7 and 9 aqueous buffers at 15°C; and (c) 5 ppm in 0.05 M pH 7 buffer at 25°C and 37°C. Solutions were thermostated and kept in the dark. Samples were taken for analysis at one week intervals for 8 weeks and applied to silica gel TLC plates, developed and radioscanned. Less than 1 percent degradation was observed in any sample. Mass spectrometeric analysis of one of the samples showed it to be the same as a reference standard. These results thus indicated that hexazinone does not hydrolyze appreciably in water.

Rhodes (10) reported on photodegradation studies of hexazinone in water under: (a) artificial sunlight having an average uv intensity at the water surface of about one-half that of typical sunshine at noon, and (b) summer sunshine in Wilmington, DE. The following solutions containing 5 ppm ^{14}C hexazinone were used:

Artificial light studies

- Distilled water (pH 6.7)
- Standard reference water (pH 8.1) corresponding to "typical" surface water in the U.S.
- Distilled water with anthraquinone (20 ppm) added as photo-initiator
- Distilled water with riboflavin (20 ppm) added as photo-initiator

Natural sunlight studies

- Standard reference water (pH 8.1)
- Standard reference water containing 20 ppm riboflavin
- Brandywine River (Delaware) water
- Brandywine River water with 2.5 cm of bottom sediments

Each solution (200 ml, 5 cm deep) was placed in a 400-ml jacketed beaker where the water temperature was maintained close to 15°C for 5 to 8 weeks. At weekly intervals, an aliquot of each sample was analyzed for total ^{14}C in the solution, and a second aliquot analyzed for ^{14}C hexazinone and ^{14}C degradation products by TLC-scintillation counting.

Tables 3 and 4 present the experimental results for the artificial and natural sunlight photodegradation tests. The results indicate that in distilled water exposed to artificial sunlight, hexazinone is slowly degraded (ca. 10 percent in 5 weeks). On the basis of 5-week data, the amount of decomposition under both artificial and natural sunlight is about three times greater in standard reference water and about four to seven times greater in natural river water or in distilled water containing 20 ppm of riboflavin. The degree of decomposition in distilled water containing 20 ppm of anthraquinone under artificial light and in natural river water with bottom sediments is about three times the amount in distilled water. At the end of the 5-week exposure period, about 10 percent of the ^{14}C in the river water with sediments was found in the sediments. Extraction of the sediments removed 67 percent of the ^{14}C. TLC analysis of the extract showed about the same distribution of ^{14}C compounds that was found in the river water, e.g., 70 percent hexazinone in the sediments and 65 percent in the water.

Based on degradation products identified, the major routes of photodegradation appear to involve demethylation to give compounds B and H (Figure 1) and hydroxylation to give compound A. The structures of these major degradation products have been previously confirmed by mass spectroscopy.

4.0 IMPACT ON NON-TARGET ORGANISMS

4.1 PLANTS

In applications of "Velpar" "Gridball" for conifer release, 0 to 15 percent conifer mortality may occur but this depends on species, rates, soil type, and other factors (6). In site preparation applications, use of high application rates can potentially result in high residue levels in the soil

TABLE 3. ANALYSIS OF AQUEOUS SOLUTIONS OF (^{14}C)HEXAZINONE EXPOSED TO UV LIGHT (% DISTRIBUTION OF RADIOACTIVITY APPLIED TO TLC PLATES) (10)

Distilled Water								Standard Reference Water										Distilled Water + Anthraquinone					Distilled Water + Riboflavin				
Exposure, Weeks								Exposure, Weeks								^{14}C Compd*	R_f†	Exposure, Weeks					Exposure, Weeks				
1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8			1	2	3	4	5	1	2	3	4	5
	1	1	2	3	3	4	5		2	4	5	6	8	10	10	Origin	0.00	1	1	2	3	4	8	15	20	25	19
	1	1	2	3	3	4	5		7	6	9	11	14	18	23	A	0.17	1	2	3	3	4	13	19	23	23	34
100	95	94	91	90	87	87	82	100	87	82	79	73	68	64	55	B, H, hexazinone	0.40	84	80	76	73	68	53	43	37	34	31
	2	2	3	3	4	5	5		2	3	4	6	6	8	7	C	0.27	4	4	6	8	11	20	15	11	10	8
	1	1	1		1		1		1	1	2	2	2		3	D	0.90	1	2		3	4	1	1		2	2
			1	1	2		2		1	4	1	2	2		2	E	0.80	9	11	13	10	9	5	7	9	6	6

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*See Figure 1 for structures.

†TLC system: ethyl acetate-methanol (9:1, v/v).

TABLE 4. ANALYSIS OF AQUEOUS SOLUTIONS OF (^{14}C)HEXAZINONE EXPOSED TO NATURAL SUNLIGHT (% DISTRIBUTION OF RADIOACTIVITY APPLIED TO TLC PLATES) (10)

Standard, Reference Water					Standard Reference Water + Riboflavin					^{14}C Compd*	R_f†	Brandywine River Water					Brandywine River Water and Sediment				
Exposure, Weeks					Exposure, Weeks							Exposure, Weeks					Exposure, Weeks				
1	2	3	4	5	1	2	3	4	5			1	2	3	4	5	1	2	3	4	5
	1	1	4		1	1	7	4		Origin	0.00			1	7	9					2
	6	3	6	6	4	6	6	11	13	A + C	0.40	6		5	14	16			1	7	6
3	4	11	11	17	6	7	10	13	16	B	0.55	3	14	17	14	18	6	9	12	10	11
	2	4	6	8	9	10	11	12	15	H	0.70		5	7	9	8		5	6	7	10
97	87	81	73	69	80	76	66	60	56	D, hexazinone	0.80	91	81	70	56	49	94	86	81	76	71

*See Figure 1 for structures.

†TLC system: chloroform-methanol (9:1, v/v).

with possible adverse impact on seedlings planted subsequently into grid spots. This possibility was evaluated very recently by the U.S. Forest Service Southern Forest Experiment Station (15) in field test plot studies with two soil types (Pacolet clay and Uchee loamy sand) in Alabama. Hexazinone ("Velpar" 90W), at 2 and 4 kg/ha, was applied by a tractor-mounted boom sprayer. Herbicide treatments were made in March/April 1978. Immediately following herbicide treatment and soil sampling, 36 nursery stock ("1-0") loblolly pine (Pinus taeda L.) seedlings were planted at 1 meter spacings in half of each plot. A similar planting was made on the remaining half of each plot in January 1979. Subsequent observation of weed control effectiveness and pine seedling injury/mortality indicated the following (15):

- Hexazinone, at 2 and 4 kg/ha, caused very high mortality and increased growth increments in surviving trees of first-year pines (i.e., those planted in 1978 immediately after herbicide treatment) on the clay soil. It also provided good weed control.
- Hexazinone at 4 kg/ha did not cause mortality but did increase growth increments of second-year pines (i.e., those planted in January 1979) on the clay soil.
- Hexazinone at both rates caused high mortality and inhibited pine growth of first-year pines in the sandy soil. However, excellent weed control was provided.
- Hexazinone at both rates did not cause pine mortality and did not significantly increase growth of second-year pines on the sandy soil.

By virtue of its pellet form and application method, aerial drift, which may impact non-target plants outside the application areas, is not expected to be a problem with the use of "Velpar" "Gridball". "Velpar" Weed Killer, soluble powder formulation containing 90 percent hexazinone, is being tested under EUP* for weed control in sugarcane fields in Florida, Hawaii, Louisiana, Puerto Rico, and Texas, and under EUP for selective weed control in alfalfa and bermuda and bahiagrass pastures.

Bush, et al. (20) measured hexazinone residues in four species of hardwoods (white oak, chestnut oak, sourwood, and hickory) cut for firewood 4 and 6 months after two mixed hardwood-pine stands in the upper Piedmont of Georgia were treated with 1.5 lb/acre a.i. of hexazinone. Individual trees were sampled at base, mid-stem, top and crown positions and subdivided into bark and wood components for moisture and residue analysis. Hexazinone residues were primarily in the form of metabolite B. The parent compound and metabolite A were found in only 7 percent of treated samples and then at concentrations less than 0.09 and 0.13 ppm, respectively. Metabolite B was detected in 19 percent of the hexazinone treated stems at maximum concentrations of 0.26 ppm in wood and 1.76 ppm in bark. The weighted total residue concentrations for both oak species were less than 0.05 ppm at all stem positions and both sampling times. In sourwood and hickory, the weighted concentrations were more variable over time and stem position, but were less than 0.15 ppm. Since the allowable residue for food crops, at which no adverse health effects will occur, is 0.2 ppm, Bush, et al. (19) concluded that the lower residues found in firewood samples would likewise produce no adverse health problems.

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*EUP = Experimental Use Permit.

The U.S. Forest Service Southern Forestry Experiment Station (Auburn, AL) is currently engaged in a study to evaluate residues of "Velpar" and metabolites in non-target fruit plants such as blackberries and blueberries; these fruits are often picked by people in the wilderness. Samples which have been collected are currently awaiting laboratory analysis (21).

4.2 AQUATIC ORGANISMS

Indirect exposure to fish and other aquatic organisms may result via runoff from sites treated with "Velpar". Acute fish toxicity data for "Velpar" Weed Killer (90 percent a.i.) submitted to EPA by DuPont indicate 96 hour TL_{50} values of 274 ppm for fathead minnows, between 370 and 420 ppm for bluegill sunfish, and between 320 and 420 ppm for rainbow trouts. These values suggest slight acute toxicity to fish (22). Data on Daphnia also suggest that the product is slightly toxic to this organism (48-hour LC_{50} is 151.6 ppm, 21-day LC_{50} is >20 and <50 ppm).

Use of "Velpar" Weed Killer in sugarcane fields in coastal areas can present a potential for exposure of shrimp, crab, and oysters. The following acute toxicity data have been reported for these organisms: grass shrimp, 56 ppm <96-hour LC_{50} <100 ppm; fiddler crab, 96-hour LC_{50} >100 ppm; and embryo larvae of oysters, 320 ppm<48-hr LC_{50} <560 ppm (22).

Rhodes (10) reported on studies to assess the potential for bioaccumulation of hexazinone in fish. Hexazinone was labelled in the 2 or 4-carbonyl position.

The ^{14}C residues (calculated as ppm hexazinone) in bluegill sunfish (mean length 63 mm, mean height 3.4 grams) exposed to water treated with 0.01 and 1.0 ppm hexazinone are shown in Table 5. The residue levels in all tissues were low and were found to plateau after 1-2 weeks of exposure. The maximum accumulation factor (^{14}C residue in fish tissue/concentration in water) of ca. 5-7 occurred in the viscera at both exposure levels. The accumulation factors in the liver and carcass were 3-5 and 2, respectively. The residue levels in all tissues decreased by greater than 90 percent after a 1-week withdrawal period in fresh water, and no detectable radiolabelled residues remained after a 2-week withdrawal period.

The major portion of the radioactivity extracted from the fish was unchanged hexazinone. The extraction procedure removed 80 percent of the ^{14}C from the fish tissue. TLC analysis showed that 91 percent of the extracted ^{14}C was unchanged hexazinone and 9 percent was 3-(4-hydroxycyclohexyl)-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-(1H,3H)-dione, a major urinary metabolite (metabolite A) of hexazinone in the rat (Rhodes and Jewell, 1980).

Mayack, et al. (18) evaluated the impact of hexazinone on aquatic macrophytes and invertebrate communities within forested watersheds in the Piedmont region of Georgia. Four replicate watersheds received hexazinone pellets (10 percent a.i.; pellet size - 2 cm^3) on April 23, 1973 and were subsequently monitored for eight months. Aquatic organisms in a second order perennial stream were exposed to intermittent concentrations of hexazinone (6 to 44 ppb). Hexazinone and its metabolites were generally not detected (0.1 ppm) in aquatic invertebrates and macrophytes (composed primarily of aquatic mosses Ecrhynchium rusciforme and Leptodictyum riparium). No major alterations in species composition or diversity were detected in the aquatic macroinvertebrate community.

4.3 SOIL ORGANISMS

Rhodes, et al. (23) reported on studies of the effect of hexazinone on bacterial and fungal populations in agricultural soils. Adding 10 ppm of hexazinone to three soils did not reduce the soil population counts of fungi or bacteria during an 8-week test period. In all soils, the distribution of a given fungus type was similar in treated and untreated soils, indicating that hexazinone did not alter the number of any given fungus component in

TABLE 5. TOTAL ^{14}C RESIDUE IN BLUEGILL SUNFISH (ppm) (10)

Exposure Period	0.01 ppm (^{14}C) Hexazinone in Water			1.0 ppm (^{14}C) Hexazinone in Water		
	Carcass	Liver	Viscera	Carcass	Liver	Viscera
3 days	0.01	0.02	0.04	1.0	1.3	2.0
1 week	0.01	0.03	0.07	1.3	1.6	5.3
2 weeks	0.02	0.03	0.07	2.1	5.0	6.7
3 weeks	0.02	0.02	0.04	2.0	2.7	5.5
4 weeks	0.02	0.02	0.05	1.0	1.9	4.6
Withdrawal Phase						
1 day	0.01	0.02	0.03	0.5	2.1	3.7
3 days	<0.01	<0.01	<0.01	<0.1	0.2	0.6
1 week	<0.01	<0.01	<0.01	<0.1	<0.1	0.2
2 weeks	<0.01	<0.01	<0.01	<0.1	<0.1	<0.1

the soil. In an agar plate bioassay test, hexazinone showed little or no fungitoxicity at treatment rates up to 100 ppm, thus indicating that hexazinone would not reduce or modify soil fungus populations at its expected use rates of 4 to 10 ppm. A nitrification study showed that the addition of 5 and 20 ppm hexazinone to two agricultural soils had no effect on soil-nitrifying process during a 5-week test period.

In their forest watershed study (see Section 4.2), Mayack, et al. (18) analyzed hexazinone residue levels in terrestrial invertebrates. In contrast to the aquatic biota, hexazinone and its metabolites accumulated in terrestrial macroinvertebrates. Mean levels of hexazinone or at least one of its metabolites were one to two orders of magnitude greater than comparable levels (0.01 to 0.18 ppm) found in forest floor material. Although this suggested an appreciable uptake of hexazinone by the microinvertebrate community either by active biological uptake or passive accumulation, the significance of the observed accumulations on the invertebrate organisms could not be established based on the limited data generated, as terrestrial microarthropod samples collected near the end of the study period (8 months after application) revealed no major community changes.

4.4 ANIMALS

DuPont (24) has carried out extensive toxicological studies of hexazinone, using rats, guinea pigs, dogs, mice, hamsters, bobwhite quail, and mallard duck. The studies included oral acute, subacute, chronic and subchronic toxicity; reproductive effects, teratogenicity; mutagenicity; skin irritation and sensitization; acute and subacute skin absorption; eye irritation; and acute and subacute inhalation. The results which are summarized in Table 6 indicate that hexazinone is of low toxicity to mammals and birds. Other data provided by DuPont (7) indicate no carcinogenic effect in a 2-year feeding study in rats; negative in bacterial and mammalian point mutation assays; not embryotoxic or teratogenic at up to 5000 ppm in diet of rat; not embryotoxic or teratogenic at up to 125 mg/kg by gavage in rabbits; and a no-effect level of 200 ppm in a 2-year rat feeding study.

TABLE 6. TOXICOLOGICAL TEST RESULTS FOR HEXAZINONE (24)

Test	Species	Test Substance	Test Procedure	Results
Acute oral	Rats (male, ChR-CD)	Unformulated	Single dose by intubation	LD_{50} 1690 mg/kg
Acute oral	Guinea pigs (male)	Unformulated	Single dose by intubation	LD_{50} 860 mg/kg
Acute oral	Dogs (male, beagle)	Formulated 90% soluble powder	Single dose in gelatin capsule	Lethal dose >3400 mg/kg (the maximum feasible dose)
Subacute oral	Rats (male, ChR-CD)	Unformulated	300 mg/kg/day by intubation, five times a week for two weeks	100% survival, no histopathological changes in tissues examined
Subchronic oral	Rats (male and female, ChR-CD)	Unformulated	Fed to weanlings for 90 days at dietary levels of 0, 200, 1000 and 5000 ppm	1000 ppm no effect level; except for decreased body weight and food efficiency, no other effects at 5000 ppm
Subchronic oral	Dogs (male and female, beagle)	Unformulated	Young adults fed dietary levels of 0, 200, 1000, and 5000 ppm for 3 months	1000 ppm no effect level; decreased body weight and evidence of liver injury at 5000 ppm
Subchronic oral	Mice (male and female, ChR-CD-1)	Unformulated	Fed to weanlings at levels of 0, 250, 500, 1250, 2500, 5000 and 10,000 ppm in diet for 8 weeks	No mortality or clinical signs of toxicity; increase in liver weight at 10,000 ppm
Subchronic oral	Hamsters (male and female engle)	Unformulated	Fed to weanling hamsters at levels of 0, 5000, 7500 and 10,000 ppm in the diet for 8 weeks	No mortality or clinical signs of toxicity
Chronic oral	Rats (male and female, ChR-CD)	Formulated 90% soluble powder	Fed to rats, starting with weanlings for 2 years	No effect level 200 ppm; lower average body weight gains, food efficiency and food consumption at 2500 and/or 10,000 ppm; hematological and urinary evidence of toxicity at only the highest level
Reproductive	Rats (male and female, ChR-CD)	Formulated 90% soluble powder	3-generation 3-litter study with rats that received 0, 200, 1000 and 2500 ppm a.i. in diet	Except for slightly lower average body weight of the pups at weaning in the 2500 ppm group, no meaningful differences among control and test groups with respect to reproduction and lactation performance
Teratogenic oral	Rats (female, ChR-CD)	Unformulated	Fed in the diet to pregnant rats from day 6 through day 15 of gestation at levels of 0, 200, 1000, and 5000 ppm	No evidence of embryotoxicity, teratogenicity or clinical signs of toxicity
Mutagenicity (Salmonella typhimurium/microsome assay)	Salmonella typhimurium	Unformulated	Ames procedure	Not mutagenic

(Continued)

TABLE 6. (Continued)

Test	Species	Test Substance	Test Procedure	Results
Skin irritation and sensitization	Guinea pigs	Unformulated	Aqueous solution (25 and 50%) applied to intact skin; intradermal injection (1%) for sensitization; challenge applications after 2 week rest periods	No skin irritation or sensitization
Acute skin absorption	Rabbits	Formulated 90% soluble powder	Single dose of 24% aqueous paste on gauze on shaved trunk area, covered with wrappings, for 24 hours	Lethal dose >5,278 mg/kg, the maximum feasible dose
Subacute skin absorption	Rabbits	Formulated 90% soluble powder	Control and test material applied daily with a syringe to a 3x3 in. 12-ply gauze pad for 10 consecutive days to clipped shoulders and back; gauze covered with PVC film and wrappings. After 6 hr. exposure each day, the film and wrappings removed and skin washed with water and dried. Nominal concentrations were 770 mg/kg/day	Elevated plasma glutamic-pyruvic transaminase activity at the highest concentration level; no such effect at lower levels; no evidence of liver or other tissue injury
Eye irritation	Rabbits	Unformulated	Right eyes of 2 rabbits treated with 10 mg powdered sample; one treated eye washed with water, the other not washed. Eyes examined up to 14 days after exposure	Moderate corneal injury and conjunctivities with no iritic effect. Eyes were normal within 7 days
Eye irritation	Rabbits	Formulated 90% soluble powder	Right eyes of six rabbits treated with 0.1 ml powdered sample; eyes examined 24, 48, and 72 hours after treatment	4/6 rabbits showed a positive reaction in at least one of the examination
Eye irritation (repeated exposure)	Rabbits	Formulated 90% soluble powder	Right eyes of rabbits treated with 1 mg powdered sample daily for up to 5 days. Eyes examined at one hour and at 1, 2, 3, 4, 5, 7 and 14 days	3 of 5 rabbit eyes had localized small areas of small corneal opacity, which was reversible. No cumulative ocular effects; all eyes normal within 3 to 14 days
Acute inhalation	Rats (male, ChR-CD)	Unformulated	One hour exposure in a chamber at 7.48 mg/l (max. that could be generated under test conditions)	LC_{50} >7.48 mg/l; 100% survival; irregular respiration and salivation during exposure
Subacute inhalation	Rats (male, ChR-CD)	Formulated 90% soluble powder (0.06% of particles in the respirable range)	Head only exposure in a chamber with an average concentration of 2.5 mg/l dust, six hours/day for 15 days with two days rest after the 5th and 10th exposure	Rats survived with no significant clinical or histopathological findings
Acute oral (wildlife)	Bobwhite quail (male and female)	Unformulated	Fed by oral intubation to fasted twenty-week old males and females at 0, 398, 631, 1,000, 1,590 and 2,510 mg/kg; birds observed for mortality and toxic effects for 14 days	LD_{50} 2,258 mg/kg
Subacute oral (wildlife)	Mallard duck and bobwhite quail	Unformulated	Fed in diet to one-month old ducks and 15-day old quail at levels of 0, 625, 1,250, 2,500, 5,000 and 10,000 ppm for the first 5 days of an eight-day study. Basal diet only was fed for the final 3 days. Dieldrin was a positive control. Birds observed daily for mortality and toxic effects	LC_{50} >10,000 ppm for both duck and quail

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Common Name: MSMA

Chemical Name: Monosodium methanearsonate

Major Trade Names: Ansar; Bueno; Daconate

Major Applications in Forestry: Used in precommercial thinning; applied by injection or cut surface.

SUMMARY

MSMA is an organic arsenical herbicide that is widely used for weed control in cotton fields. In forestry, it is used to thin conifers by injection or by application on cut tree surfaces, but the total amount used in forestry is a small fraction of the agricultural use. The primary environmental concern in the use of MSMA is arsenic toxicity. MSMA itself is less toxic to most animal species than is inorganic arsenate, the primary breakdown product. MSMA is converted to several other organic and inorganic arsenicals in the environment. However, MSMA and all of these products occur naturally in soils, in water and in the tissues of organisms. Furthermore, the amount of MSMA annually produced and used in the United States is a small fraction of the amount of arsenic that occurs naturally in the soil.

In most surveys, agricultural use of MSMA has not resulted in a significant increase above the background arsenic content of soil. The major breakdown product of MSMA in soil is inorganic arsenate which is relatively quickly and tightly bound in soil. Therefore, entry of MSMA into soil does not significantly increase the risk of contamination of drinking water by the leaching of arsenic from soil. In forestry, arsenic from MSMA use enters the soil when foliage of treated trees decomposes, and no contamination of streams by this arsenic has been detected. Arsenic does accumulate in the tissues of organisms. However, in animals, it tends to achieve the highest concentrations in species at the bottom of food chains, and it does not appear to biomagnify in food chains.

MSMA is toxic to some agricultural crops such as soybeans when applied at the rate used on cotton plants. It is moderately toxic to rabbits and to cattle. It has low toxicity to fish and birds, and it has moderate toxicity to honey bees when they are sprayed or when they ingest contaminated food. Proper use of MSMA in forestry is unlikely to harm wildlife or domestic animals. However, spraying MSMA on foliage accessible to grazing animals can endanger both domestic and wild species.

1.0 INTRODUCTION

MSMA is the most widely used organic arsenical herbicide. It is generally applied at low rates and has the lowest mammalian toxicity of the arsenical pesticides (1). However, MSMA is a potential hazard to a wide spectrum of organisms since it breaks down to form inorganic arsenate that is toxic to both plants and animals.

The biological activity of MSMA was known prior to 1900 but MSMA was not used as a herbicide until 1951 (1). At present, MSMA is used primarily in agriculture to control post-emergent weeds in cotton. It is also used as a nonselective herbicide against grasses in noncrop areas such as ditchbanks, right-of-way and storage yards (2). Forestry use is by injection or cut surface application to unwanted trees for site preparation, for brush control of weed trees over 2 inches in diameter and especially for precommercial thinning of hardwoods and conifers (3,4).

United States consumption of MSMA in 1972 was estimated at 19 million pounds (5). Industrial and commercial use, which includes forestry applications, amounted to 4 million pounds, about 21 percent of total use. About 66 percent or 12.5 million pounds were used in agriculture, primarily in the south-central states; home and garden uses amounted to 1.5 million pounds and various uses by governmental agencies accounted for 1.0 million pounds.

MSMA is manufactured by several chemical companies. The principal U.S. producers are Diamond Shamrock Company and Vineland Chemical Company (6). MSMA is available in several formulations under numerous trade names. Some of the common formulations are listed in Table 1. The forest industry generally uses a 50 percent solution (6 lbs per gal) with approximately 22 percent total arsenic content (7). Those formulations with surfactants are used primarily in agriculture as foliar sprays.

MSMA was first used as a foliar spray against crabgrass in turf. It is now known to be effective against several grasses. In cotton and on noncrop lands, MSMA is used to control Johnsongrass, nutsedge, watergrass, sandbur, foxtail, cocklebur, and pigweed (1,6). In forestry, MSMA is applied only in spot treatment of trees by the cut surface (hack and squirt) or injection methods. It is effective against Douglas-fir, lodgepole pine, bigleaf maple,

TABLE 1. SOME COMMON FORMULATIONS OF MSMA (1,2,6,7,10-16)

Trade Name	MSMA		% Total Arsenic	Other Chemicals Present	Manufacturer
	lb/gal	%			
Ansar 529	4.0	35%	16%	surfactant	Diamond Shamrock
Ansar 529 H.C.	6.0	48%	22%	surfactant	Diamond Shamrock
Bueno 6	6.0	48%	22%	surfactant	Diamond Shamrock
Daconate	4.0	35%	16%	surfactant	Diamond Shamrock
Ansar 70 H.C.	8.0				Diamond Shamrock
Silvisar 550*	6.0	48%	22%	—	TSI Company
Weed-E-Rad+W	4.02	35%	16%	surfactant	Vineland Chemical
Dal-E-Rad+W	4.02			surfactant	Vineland Chemical
Weed-Hoe 120	6.67				Vineland Chemical
Weed-Hoe 2X	8.0				Vineland Chemical
Check-Mate				surfactant sodium cacodylate	Vineland Chemical
Diumate				diuron	Crystal Chemical
Broadside				surfactant sodium cacodylate	
Panther Juice	4.0	35%	16%	surfactant	MFC Services (AAL)
Valson 6.6	6.6	51%	24%	—	Valley Chemical
MSMA 4 Plus	4.0	35%	16%	surfactant	Grower Service

*Discarded name as of 1980 (6).

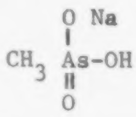
ponderosa pine, and certain types of alder, ash, cedar, elm, oak and cherry (4,8). Its major use is in precommercial thinning of overdense stands to promote more rapid growth of timber (9).

Forest application of MSMA utilizes undiluted herbicide usually at a concentration of 6 lbs per gallon, and the cost in 1979 was $14.50 per gallon (6 lbs a.i.). Several cuts are made into the cambium of the tree, the number depending on the size of the trunk (7). One or two ml of MSMA are applied per cut. The season of application is fall and winter. The MSMA is translocated throughout the plant (1). It is slow in killing the tree, producing first a chlorosis and the cessation of growth. Gradual yellowing of leaves occurs, then the yellow leaves become brown, followed by dehydration and death (1). The specific mode of action of MSMA is not known with certainty, but it appears to interfere with phosphorus metabolism in plants (17). To be effective, the chemical must contact leaf surfaces in use as a spray or be injected into the growing part of the tree.

MSMA has been used in the forests of the Pacific Northwest for precommercial thinning (18). Approximately 41 thousand pounds were used to thin about 28 thousand acres of U.S. Forest Service land in Oregon, Washington, and California from 1975 to 1979 (19). MSMA is not used extensively in the southeastern United States. Some 624 pounds were used to thin 165 acres of USFS trees in the southeast in 1979 (20). The amounts of reported use and the mode of application indicate that environmental contamination due to MSMA in forests should be minimal and generally limited to the immediate area of the treated trees.

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF THE ACTIVE INGREDIENT

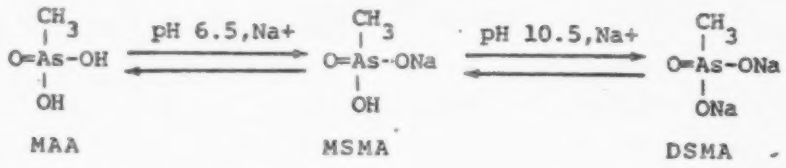
MSMA, monosodium methanearsonate, has the structure:



$$\mathrm{CH_3}\ \overset{\mathrm{O\ Na}}{\underset{\mathrm{O}}{\mathrm{As}}}\mathrm{-OH}$$

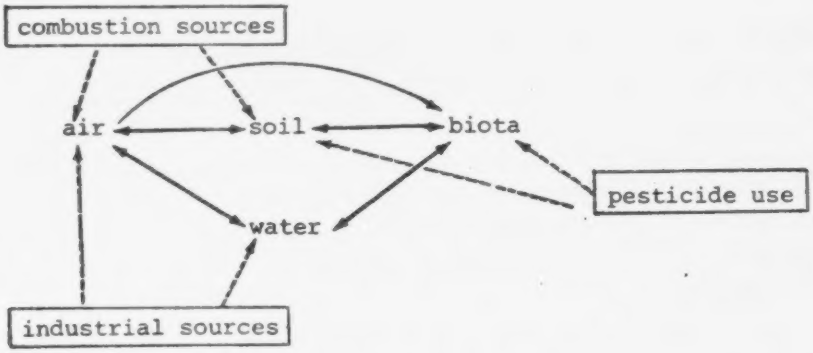
It belongs to a group of organic arsenical herbicides that are salts or derivatives of methanearsonic acid. Other members of this group include cacodylic acid, disodium methanearsonate, octyldodecyl ammonium methanearsonate and calcium acid methanearsonate.

Aqueous solutions of MSMA are clear to light yellow and are odorless. MSMA is an acid in aqueous solution and is in equilibrium with methanearsonic acid (MAA) at pH 6 to 7. At pH 10 to 11, the equilibrium is shifted toward formation of the disodium salt (21):



MSMA is highly stable in water, but in the presence of calcium, magnesium or iron, it will form insoluble salts of these ions (6,21).

The effectiveness of MSMA and like compounds is due to the arsenic atom. Although often referred to as a heavy metal, arsenic is not a heavy metal or a true metal, but is a metalloid with metallic and non-metallic properties (1). Arsenic can be found in valence states from +5 to -3. It is ubiquitous in nature being found in all environmental substrates (1,22). Arsenic cycles in the environment; it is taken up and released by biota and sediments and soils; low concentrations are maintained in air and water (22). The following diagram is a schematic presentation of the arsenic cycle in nature; solid lines represent natural transfers; dashed lines represent anthropogenic inputs (22):



3.0 ENVIRONMENTAL FATE

The fate of MSMA in the environment has been determined primarily from field studies measuring total arsenic residues and from laboratory studies of microbial degradation. Methods are now available to distinguish between MSMA, cacodylic acid, As^{+3} and As^{+5} (21,23). However, due to the difficulty of separation, the analyses that are normally performed measure all forms of arsenic, as total arsenic, and do not differentiate between organic and inorganic arsenic.

Natural arsenic levels in air and water are generally low; soil residues, however, can cover a wide range. The following are reported background levels of total arsenic (22):

- Soil	1 to 40 ppm, from weathered rock
- Freshwater	0.5 to 2.3 ppb, Lake Michigan
- Sea Water	0.15 to 6.0 ppb
- Air	10 $\mu gm/m^3$, rural air 30 $\mu gm/m^3$, urban air

Background levels can reflect natural and anthropogenic sources of arsenic. The higher value for urban air is due to pollutant emissions from industrial and combustion sources (22).

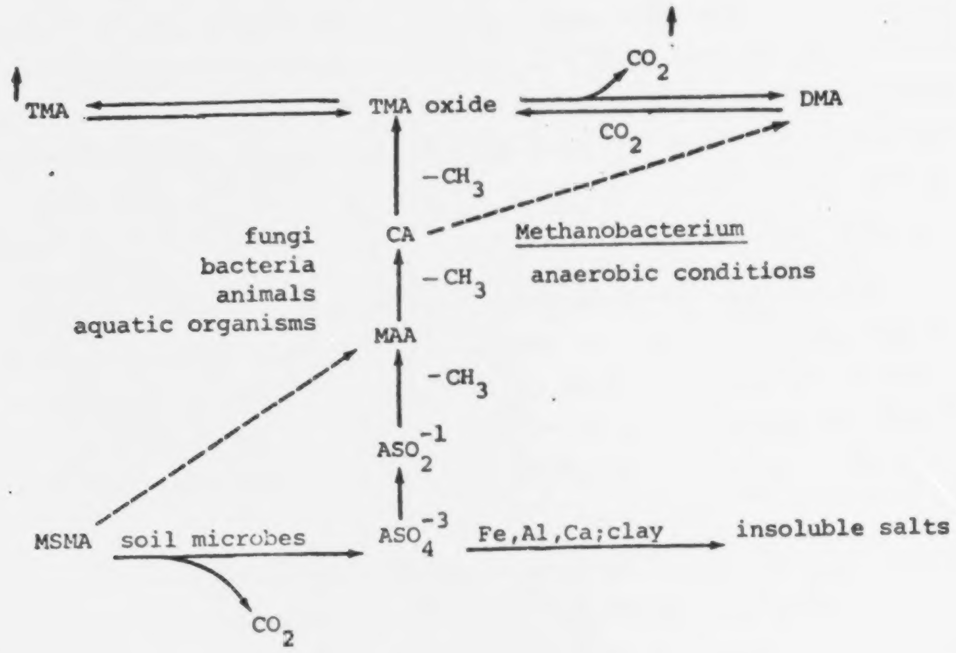
Estimates of the magnitude of various anthropogenic sources of arsenic are found in Table 2. Emissions from copper smelters are the largest anthropogenic source, but agricultural use is a significant fraction of the total. The amount of arsenic used in forestry is estimated to be less than 0.1 percent of the total arsenic released by man.

TABLE 2. COMPARISON OF VARIOUS ANTHROPOGENIC SOURCES OF ARSENIC

Source	Metric Tons Per Year
Total airborne losses from the smelting of copper ores, nationwide (24)	4800
Total airborne losses from coal burning, nationwide (24)	650
Total agricultural consumption of MSMA-arsenic in 1972, nationwide (assuming use of MSMA with 16% arsenic content) (5)	910
Total industrial and commercial (including forestry) consumption of MSMA-arsenic in 1972, nationwide (assuming use of MSMA with 24% arsenic content) (5)	440
Total reported annual use of MSMA-arsenic, based on USFS reports (19,20)	1
Total estimated annual forestry use of MSMA-arsenic (assuming total reported USFS use is 20% of total forestry use)*	5

*In 1970, USFS lands comprised about 20 percent of all U.S. commercial forest land (25).

Arsenate and CO_2 are products of the microbial decomposition of MSMA. Arsenate is reduced and methylated to volatile compounds by various organisms in the environment. The components of an environmental fate analysis of MSMA include arsenate, methylated arsines, cacodylic acid and other organic arsenicals. All of these compounds are naturally occurring; all of them are products of or substrates for natural microbial transformations. The major pathways in the environmental chemistry of MSMA are shown in the following diagram (see Section 6.0 for chemical structures):


TMA
TMA oxide
DMA
CO2
CO2
-CH3
CA
Methanobacterium
anaerobic conditions
fungi
bacteria
animals
aquatic organisms
-CH3
MAA
-CH3
ASO2 -1
MSMA
soil microbes
ASO4 -3
Fe,Al,Ca;clay
insoluble salts
CO2

The major environmental concern in regard to MSMA is the fact that it is largely converted to arsonate in soil which cannot be further degraded and is much more toxic than the organic compound. Toxic trimethylarsine gas (TMS) can also be produced from the inorganic arsenic. The degradation products of MSMA, largely arsonates, are very persistent in the soil with a half-life of approximately 6 years (22).

3.1 UPTAKE AND METABOLISM BY PLANTS

Uptake and metabolism of MSMA by plants have been studied primarily in agricultural systems. Information does not appear to be available on the metabolism of MSMA injected into trees. MSMA in Johnson-grass is rapidly taken up by the roots and is translocated throughout the plant in 4 hours (1). Atrazine has been shown to facilitate the uptake of arsenic by plants. Temperature is also a factor in translocation and toxicity in plants. MSMA sprayed on cotton at 3 lbs per acre caused injury to the plants when applied at 13°C or 20°C but not at 31°C (1,25,26). Maximum absorption was observed at 29°C; translocation out of the cotyledons was faster at 20°C than 29°C.

Some plant species are able to metabolize MSMA. One or more metabolites containing arsenic were found in target plants possibly involving formation of a histidine complex (1,27). However, some 40 percent of MSMA in beans remained unmetabolized and no metabolites were found in cotton 72 hours after exposure, indicating that most MSMA may remain unmetabolized in non-target plants.

3.2 FATE IN SOIL

MSMA reaching the soil can undergo several physical, chemical, and microbial reactions. MSMA in soil is largely broken down to inorganic arsenate. Formation of insoluble salts, adsorption, ion exchange and microbial transformations are all possible reactions of MSMA in soil. MSMA itself is a chemically stable compound and is not known to volatilize or photodecompose (21).

Direct entrance of MSMA into soil due to forest application would result primarily from splash back in hack and squirt applications and from leakage of equipment in injection methods. Proper handling to avoid spillage and care in disposal of wash water and empty containers should minimize the potential for environmental contamination. Concentrations of arsenic in forest litter following use of MSMA for tree thinning has been reported to range from 1.8 to 39 mg per kg (28). Contamination due to splash back and leakage of MSMA can spread from the area of the treated tree through leaching and runoff. A substantial source of MSMA-derived arsenic in forest soils appears to be arsenic-containing foliage that falls to the ground after treatment. Newton (29) measured 116 ppm arsenic in dead pine needles several months after application.

3.2.1 Soil Residues

Naturally occurring arsenic residues in soil usually range from 1 to 40 ppm (22). The National Soils Monitoring Program found arsenic in over 99 percent of sites tested in 1969 (30). The range of values was 0.25 to 107.45 ppm. The arsenic appeared to be largely from natural sources; only 0.5 percent of the sites tested reported using MSMA that year.

Hiltbold, et al. (31) measured soil arsenic residues due to applications of up to 35.6 lb per acre of MSMA (10 times the normal rate). MSMA was applied to cotton as a broadcast spray with a cumulative maximum dose of 100 lb per acre. Thirty-nine to 67 percent of the applied arsenic was detected as soil residues in the top 30 cm of soil. The rest of the applied arsenic was thought to have escaped to the air by formation of volatile arsine gas. No residues were found below 30 cm. Increased adsorption was observed with increasing depth and corresponding increases in clay and iron content. Robinson (32) investigated the effects of application of large amounts of MSMA over a period of 5 years. Soil residues were measured to a depth of 90 cm. Surface soil residues were not significantly different from the control for application rates of up to 32 lb per acre. Rates of 64 lb per acre and up resulted in increased surface arsenic residues after the second year of application. For the higher application rate of over 250 lb per acre, 50 percent of the arsenic applied was recovered in the upper 10 cm of surface soil. Even after 5 years, arsenic residues below 30 cm were not significantly different from the control. For the soil tested, a sandy loam, use of the normal field rates of MSMA did not increase soil arsenic residues significantly.

A similar study was done by Johnson and Hiltbold (33). MSMA was applied at cumulative rates of up to approximately 60 lb of arsenic per acre. Most of the arsenic applied was recovered in the upper 5 cm of the soil. 85 percent of these surface soil residues were found in the clay fraction of the soil. Very little organic arsenic was found in the soil.

Woolson, et al. (34) measured arsenic residues in surface soil samples taken from treated and untreated soils in several states. Soils with a history of arsenic application averaged 165 ppm; untreated soils averaged 13 ppm. Samples were also taken to a depth of 1.82 m. Most of the arsenic found was in the first 15 cm of soil but arsenic was found in all of the samples. Most of the arsenic was associated with iron; lesser amounts were associated with aluminum and calcium. The recovery of applied arsenic was least in areas where silting and flooding occur.

3.2.2 Adsorption and Leaching

Norris (35) reported that MSMA is moderately mobile in forest soil and forest floor material. About 80 percent of MSMA was not retained in a 6-inch column of forest floor material; about 50 percent applied to a 3-inch soil column was not retained.

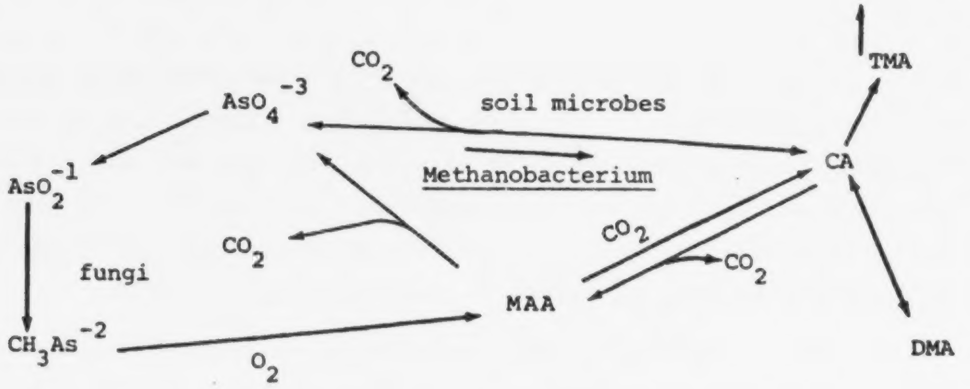
Arsenic bound to soil is said to be fixed. Physical adsorption, ion exchange reactions and formation of insoluble salts can all result in the fixation of arsenic in soil. It is not always possible to determine which mechanism of fixation is responsible for the observed association of arsenic with clay or cations as insoluble salts. Arsenic can react with iron and aluminum oxides which coat clay particles or react with cations in the soil solution (22). Adsorption of arsenic to clay depends upon soil pH, texture, iron and aluminum content, and organic matter. There is always some arsenic present in the soil solution and is likely that which is available for microbial transformations (22). Fixed arsenic is apparently unavailable for uptake by plants since phytotoxicity is generally reduced by the fixation of arsenic (1).

3.2.3 Microbial Transformations

Microbial transformations play a major role in the fate of MSMA arsenic in soil. Soil microorganisms have been shown to degrade MSMA (36). Fungi and bacteria as well as some animals and aquatic organisms are capable of producing methylated arsines from inorganic arsenicals (22).

Von Endt, et al. (36) studied microbial degradation in various types of soil using CO_2 evolution as the measure of decomposition. After three weeks incubation, the amount of CO_2 evolved was dependent on organic matter content. About 10 percent was evolved from a 3.9 percent organic soil and only 1.7 percent from a 1.7 percent organic soil. Steam sterilization of the soil resulted in almost no CO_2 evolution, indicating that microbial metabolism was responsible for MSMA decomposition. A fungus, two actinomycetes and a bacterium that were isolated from the soil all produced CO_2 and arsenate as the sole products of MSMA degradation.

Several organisms in the environment have been shown to methylate arsenicals, forming volatile compounds. Cox and Alexander (37) isolated three sewage fungi capable of producing trimethylarsine gas (TMA). McBride and Wolfe (38) have shown that cell extracts of Methanobacterium form dimethylarsine (DMA) from arsonate under anaerobic conditions. The requirements are the same as those for synthesis of methane gas indicating a competition between arsenate and substrates for methane synthesis. The methylated arsines produced are volatile and toxic but also unstable and probably react to form oxides (22,38,39). The methylation and demethylation of arsenicals in soil can be illustrated as follows (1,38):



Methylated arsenicals have also been found in the environment in places other than in soil. Bramen and Foreback (39) found low levels of methanearsonic acid (MAA) and dimethylarsinic acid (CA) in natural waters, bird eggshells, seashells and human urine. Because dimethylarsine is easily oxidized, it could not be determined in the laboratory. Woolson (22) reports that MAA and CA have been found in fresh and salt water, aquatic weeds and shrimp. Di- and trimethyl-arsine gases have been measured in outdoor and indoor air.

3.3 FATE IN WATER

Many of the arsenic reactions that occur in soil also occur in natural waters and in bottom sediments. Inorganic arsenic exists in oxygenated water primarily as arsonate (22). Insoluble salts may form. Adsorption to clay particles and methylation can also occur in water or sediment. Certain marine bacteria are capable of reducing arsenate to arsenite (22). Methylation reactions to form MAA, CA, DMA and TMA occur in both fresh and salt water.

Arsenic residues in natural waters are generally low (22). A survey of U.S. surface waters reported 79 percent of waters sampled had arsenic residues less than 10 ppb, the recommended drinking water standard, and only 2 percent had residues greater than 50 ppb. The concentration in water is generally less than that of the sediment. For example, Lake Michigan water had residues of 0.5 to 2.3 ppb and the sediment had residues of 7.2 to 28.8 ppm (22).

MSMA used at the rate of 5 lb per acre to control weeds along irrigation canals was found not to contaminate the water (40). Maximum residues of 0.86 ppm were found immediately after treatment and were reduced to 0.06 ppm or less in 10 minutes. It was calculated that 0.002 to 0.04 lb of arsenic per acre could reach farmland from a 24-hour 6-inch irrigation. These figures are well within the range of naturally occurring arsenic levels.

Canutt, et al. (18) monitored arsenic in forest streams after injection of MSMA for precommercial thinning. No residues were detected in streamwater. The limit of detection was 0.01 ppm.

4.0 IMPACTS ON NON-TARGET ORGANISMS

Concern for non-target organisms exposed to MSMA is due to the presence of arsenic. Oral LD_{50}'s in rats range from 700 to 1800 mg/kg, indicating moderate toxicity (41).

4.1 PLANTS

As noted in Section 1.0, the herbicide MSMA is used against hard-to-control grasses and weeds. As a tree killer, it is used against hardwoods and conifers. In agriculture, MSMA is widely used to control weeds in cotton fields. It is applied when cotton is at least 3 inches high but before first bloom to avoid arsenic accumulation in the seeds (31). Slight burning and a reddish discoloration of the cotton leaf may occur but the plant develops normally (2). Wauchope and McWhorter (42) designed a field experiment to simulate spray drift conditions to which soybeans may be exposed when grown in fields adjacent to cotton. Injury to soybean plants and a significant reduction in yield resulted from application of 5 to 20 percent of the normal application rate of MSMA to cotton (2 lb per acre applied four times per season). A series of experiments were used to study the effects of MSMA on grasses of a salt marsh (43). Leaf damage was noted at the higher doses of

100 and 9000 ppm applied several times as a foliar spray. A flooding experiment simulated actual conditions if MSMA were present in tide water. Doses of 10,000 and 90,000 ppm caused tissue damage on shoots. The amounts of MSMA causing plant injury were massive compared to the concentrations likely to be present in tide water due to runoff from treated areas (43).

Arsenic is normally found in plants at about 4 ppm in dry weight of plant material (21). The arsenic level in the soil that will be phytotoxic depends upon the chemical form of the arsenic, the soil fertility, amounts of iron and arsenic in the soil and plant vigor. In one case, 250 ppm in the upper 6 inches of soil resulted in a 50 percent reduction in growth of 4-week-old corn plants (21). Residues of 10 ppm of arsenic were measured in plant material.

Wauchope and McWhorter (42) studied MSMA in soybeans. Foliar application of as little as 0.4 lb per acre for the season resulted in plant injury and decreased yield. MSMA applied early in the season did not result in recoverable residues in soybeans. However, MSMA applied late in the season accumulated in the seeds. This application was only 5 percent of the normal foliar spray. According to other investigators, a concentration of 120 times the normal rate would be required in soil to result in residues in seed (42).

4.2 FISH AND OTHER AQUATIC ORGANISMS

MSMA has relatively low toxicity to fish with 96-hour LC_{50}'s ranging from 13 to 1,100 ppm (21,44). The acute toxicity of MSMA depends upon the fish species and the amount of arsenic in the formulation. Table 3 lists LC_{50}'s for various fish. The movement of large amounts of arsenic from treated areas to water containing fish is not likely to occur due to fixation of MSMA in plants, soil and sediment (1).

MSMA appears to have little toxicity to certain aquatic organisms. Shrimp and oysters were exposed to 1 ppm MSMA in flowing sea water (21). No adverse effects were observed in shrimp in 48 hours nor in oysters exposed for 24 hours. A 96-hour exposure to 100 ppm was not toxic to scud, a freshwater crustacean (21).

TABLE 3. ACUTE TOXICITY OF MSMA TO VARIOUS FISH (21,44)

Fish	% a.i. in Formulation	LC_{50}, ppm	Exposure Time in Hours
Bluegill	34.7 34.8	49.2 >1,000	96 48
Channel catfish	34.7 100	26.8 1,100	96 96
Fathead minnow	100	13.3	96
Goldfish	100	31.1	96
Rainbow trout	22.6	96.0	96
Black bass	100	700	96
Crayfish	100	3,050	96

4.3 WILDLIFE AND DOMESTIC CATTLE

In general, MSMA appears to be relatively non-toxic to wildlife. The oral LC_{50} for ducks is greater than 5000 ppm (45). Mallard ducklings and bobwhite quail were fed up to 464 ppm of a 51.3 percent MSMA formulation for 5 days; one group was given a single dose of 5000 ppm. No toxicity symptoms or abnormal behavior were observed.

Wildlife was sampled for tissue residues after forest application of arsenicals including MSMA (46). The reported results placed the animals in two groups: those in which there were generally no detectable residues and those in which low levels of arsenic were found. Essentially no residues were detected in several species of birds, mountain beaver, porcupine, ruffled grouse and one deer known to be a resident of the area. The low level group consisted of voles, shrews, mice, chipmunks and ground squirrels. About 50 percent of this group had arsenic residues between 0.5 and 9.8 ppm; most of the animals had residues below 5.0 ppm. One squirrel had 17 to 30 ppm arsenic in various body parts. Animals collected more than 30 days after herbicide injection generally exhibited no detectable residues. Two hares examined 2 and 42 days after forest treatment with arsenicals had no arsenic residue;

five hares examined 232 days after application had very low levels or no residues. The MSMA LD_{50} for snowshoe hares is reported as 173 mg/kg (46).

MSMA toxicity to rabbits was investigated more fully by Exon, et al. (47). Rabbits were fed 50 ppm MSMA (27.5 ppm arsenic) for 17 weeks. This concentration in the feed resulted in an average dose of 1.5 mg As/kg body weight. At intervals, rabbits were sacrificed and various tissues examined for arsenic residues and pathological changes. Table 4 lists the residue found in various tissues and organs. After 14 days exposure, a 35 percent decrease in food intake was observed along with intestinal inflammation and congestion (48). Several rabbits developed toxic hepatitis after 7 weeks exposure. When the MSMA dose was reduced to 0.74 mg As/kg at 17 weeks, toxic hepatitis was not found and yet residues in the liver increased. The toxic hepatitis may have blocked arsenic accumulation in the liver. Tests on offspring showed no residues at 1 and 20 days of age. A high proportion (70 percent) of the arsenic was excreted in feces and urine.

TABLE 4. ARSENIC RESIDUES FOUND IN RABBITS, PPM (47)

Tissue or Organ	Weeks of Exposure					
	0	2	4	7	12	17
Liver	0.20	0.57	0.37	0.44	0.37	0.78
Kidney		0.56	0.47	0.56	0.49	1.40
Muscle		--	0.27	0.26	0.54	0.36
Bone		--	--	--	--	3.52
Hair	0.70	--	1.30	2.42	3.58	2.29
Feces		11.30	8.10	8.50	8.80	8.40
Urine	--*	15.10	9.10	13.30	8.40	6.20

*--: below the limits of reliable detection

Cattle are often allowed to graze in forested areas treated with MSMA. Exposure to arsenic has been measured as residues in hair and other body tissues. Norris (49) compared arsenic residues in cattle hair before and after forest treatment (spring and fall) in a herd with previous exposure to arsenicals. Arsenic residues in a control herd having no previous exposure were also measured in the spring and fall. There was no statistically significant difference between spring and fall arsenic residues for the test herd. The spring average was 0.69 ppm and the fall average was 0.48 ppm. However, there was a statistically significant difference between spring and fall residues for the control herd (0.16 ppm spring, 0.35 ppm fall). The cattle grazed in untreated areas over the summer naturally accrued some arsenic as residue in hair. All the residue values obtained appeared to be within the normal range of up to 2.7 ppm for cattle as shown by other studies (49,50).

Dickinson (50) orally administered 10 mg MSMA per kg to cattle for 8 to 10 days. Four of five test steers died; their body tissues were examined for gross pathology and arsenic residues (see Table 5). The examination revealed massive kidney damage, evidence of hemorrhagic gastritis and lesions in the liver of one steer. The steers that were on a regular diet for 2 to 8 days had reduced arsenic residues in kidney and liver and yet had extensive kidney tissue damage. The damage to the kidney was apparently irreversible and was considered to be the cause of death. Cumulative doses of 80 to 100 mg/kg were fatal to 4 of the 5 cattle; poisoning occurred in all 5 cattle with a total dose of 50 to 70 mg/kg. Arsenic residues in body tissues did not always give a true indication of the effect of MSMA on the animals.

TABLE 5. ARSENIC RESIDUES AS PPM IN CATTLE ORALLY ADMINISTERED 10 mg MSMA/kg (50)

Exposure	Days on Regular Diet Prior to Exam	Body Tissue						
		Kidney	Liver	Brain	Bone	Muscle	Stomach	Hair
0	0	0.25-1.1	0.7-0.82	0.05	0.03	0.02	0.02	0.81-2.7
10	0	58	27	1.8	5.0	10		3.3
10	2	27	27	2.6	2.5	7.4	14	1.4
8	0	46	18					
8	8	3.5	1.6					

Evaluation of the studies to determine the impact of MSMA on cattle indicate conflicting results. A reliable method to measure exposure of cattle to MSMA had not yet been developed; measurement of residues in hair and body tissues appear to be unsatisfactory.

4.4 BENEFICIAL INSECTS

Studies of the toxicity of MSMA to beneficial insects generally deal with honey bees. There is some controversy over the effects of MSMA on bees. Some investigators indicate that the main hazard of herbicides including MSMA to bees is loss of pollen and nectar plants (53). The response of bees to MSMA in laboratory studies appears to depend upon the formulation and method of application.

Atkins, et al. (54) report a 48-hour LD_{50} for bees of 24 μg MSMA per bee. Pesticides with LD_{50}'s of 11 μg or more per bee were considered non-toxic. MSMA was applied as a dust in this study. Johansen (55) states that queenless hives observed in the fall have been associated with use of arsenicals the preceding summer. Morton, et al. (56) investigated the effects of arsenicals as stomach poisons fed to bees at 10, 100 and 1000 ppm in 60 percent sucrose for 60 days. A commercial formulation of MSMA, Ansar 170, was shown to be toxic to bees at all three concentrations. The time necessary to kill one-half of a given population was as follows for Ansar 170:

ppm Ansar 170	$t_{1/2}$, days
0	39.5
10	29.5
100	5.4
1000	2.5

The toxicity of various arsenicals tested was not affected by addition of surfactants.

Moffett, et al. (53) studied the effects of MSMA sprayed onto bees in cages. The bees were sprayed once with a concentration equivalent to the normal field application rate of 4 lb per acre. Dead bees were counted every day. MSMA was found to be extremely toxic with 65 percent cumulative mortality in 3 days.

4.5 MICROORGANISMS

The effects of MSMA on microorganisms are varied. High concentrations appear to inhibit bacterial growth. Arsenicals as a group are more toxic to bacteria than fungi with the greatest toxicity exhibited by organic arsenicals (57). Bollen, et al. (58) studied the response of bacteria, actinomycetes and fungi to MSMA in concentrations up to 10,000 ppm. Bacterial growth in liquid culture media was inhibited at 10,000 ppm and slightly inhibited at 1000 ppm. The rate of microbial decomposition of organic matter in the soil in the presence of MSMA was also measured as CO_2 evolution from soil and forest floor material. The rate of CO_2 evolution due to microbial decomposition in soil generally decreased with time. MSMA at 100 ppm inhibited decomposition in soil and forest litter; at 1000 ppm MSMA actually increased decomposition in soil.

Bollin, et al. (28) investigated the effects of MSMA on nitrogen metabolism in soil and forest floor material. Ammonification was enhanced by the presence of MSMA. Nitrification, however, was inhibited by as little as 10 mg arsenic per kg soil or forest litter.

5.0 BIOACCUMULATION

Because MSMA is an organic arsenical and is converted to other organic arsenicals in the environment, there is concern that these forms will bioaccumulate in organisms and perhaps biomagnify in food chains. Some marine organisms, especially algae, accumulate arsenic up to 142 ppm (52). Arsenic in these organisms is probably incorporated as organic compounds or is bound to cell walls. Fish and algae are apparently capable of synthesizing lipid-soluble and water-soluble organic arsenic compounds (52). However, concentrations of arsenic are usually highest in lower members of aquatic food chains, and arsenic does not appear to biomagnify (1).

Isensee, et al. (51) investigated the accumulation of dimethylarsine (DMA) obtained from soil in algae, snails, Daphnia and fish. Two systems were used to recover DMA from soil: an oxygen system and a nitrogen system. DMA is easily converted to the oxidized form, cacodylic acid, in the presence of oxygen. The nitrogen system was used to minimize this conversion. Table 6 lists bioaccumulation ratios for both recovery systems. DMA concentration in the aquarium water was 7.0 ppb 24 hours after its addition. Ratios for lower aquatic organisms were much higher than those for fish.

TABLE 6. BIOACCUMULATION RATIOS FOR AQUATIC ORGANISMS EXPOSED TO DIMETHYLARSINE (51)

Treatment	Algae	Snails	Daphnia	Fish
DMA oxygen recovery	1605	446	2175	19
DMA nitrogen recovery	1248	299	736	49

Woolson, et al. (52) studied bioaccumulation of MSMA and inorganic arsenic in aquatic organisms. Crayfish were found to store substantial amounts of arsenic whereas catfish did not. Crayfish placed in water that was nearly arsenic-free did not lose all the arsenic residue in body tissues. Some arsenic was either tightly bound or assimilated into cellular components. Lipid incorporation was generally higher for MSMA than for inorganic arsenic. Table 7 presents the data from these experiments. At least four stable arsenic compounds were found in body tissues, suggesting that these organisms metabolized MSMA.

TABLE 7. BIOACCUMULATION PARAMETERS FROM AQUATIC ORGANISMS EXPOSED TO MSMA ARSENATE (52)

Parameter	Daphnia	Gambusia	Algae	Crayfish
Exposure	29 days	15 days	27 days	12-15 days
Inorganic As in organism, ppm	3.6 ppm	101.9 ppm	26.9 ppm	4.3 ppm
BR* for As	5	127	34	5
As % lipid soluble	20%	86%	2.5%	20%
MSMA in organism, ppm	8.4 ppm	108 ppm	4.2 ppm	1.4 ppm
BR* for MSMA	8	110	4	1
MSMA % lipid soluble	29%	42%	17%	27%

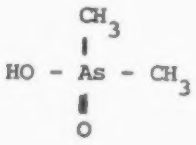
*BR = bioaccumulation ratio

6.0 GLOSSARY OF CHEMICAL TERMS

Arsenate: inorganic arsenic radical where arsenic has a valence of +5; AsO_4^{-3}

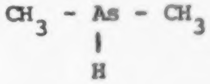
Arsenite: inorganic arsenic radical where arsenic has a valence of +3; AsO_2^{-1}

Cacodylic acid(CA): hydroxydimethylarsine oxide; dimethylarsinic acid; here arsenic has a valence of +1; $(CH_3)_2AsO_2H$; an organic arsenical herbicide, also a naturally occurring compound;



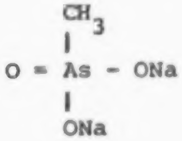
$$\begin{array}{c} CH_3 \\ | \\ HO - As - CH_3 \\ \| \\ O \end{array}$$

Dimethylarsine (DMA): an alkylarsine where arsenic has a valence of -3; $(CH_3)_2AsH$; a naturally occurring compound produced by organisms from arsenate;

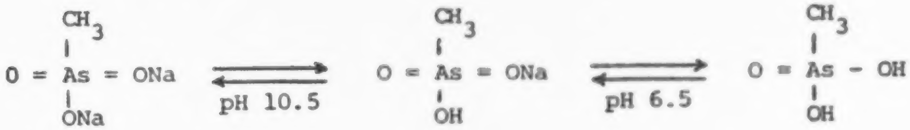


$$CH_3 - \underset{\displaystyle H}{As} - CH_3$$

Disodium methanearsonate (DSMA): at pH 10.5, DSMA is the predominant sodium salt of methanearsonic acid (MAA); DSMA is an organic arsenical herbicide, also a naturally occurring compound at high pH; $Na_2AsO_3CH_3$;



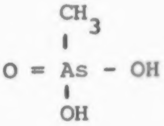
$$O = \overset{\displaystyle CH_3}{\underset{\displaystyle ONa}{As}} - ONa$$



$$O = \overset{\displaystyle CH_3}{\underset{\displaystyle ONa}{As}} = ONa \underset{pH\ 10.5}{\rightleftharpoons} O = \overset{\displaystyle CH_3}{\underset{\displaystyle OH}{As}} = ONa \underset{pH\ 6.5}{\rightleftharpoons} O = \overset{\displaystyle CH_3}{\underset{\displaystyle OH}{As}} - OH$$

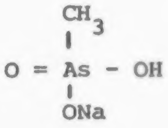
DSMA MSMA MAA

Methanearsonic acid (MAA): methyl arsonic acid; $CH_3AsO_3H_2$; an organic arsenical herbicide; also a naturally occurring compound at low pH;



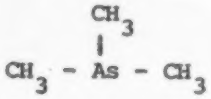
$$O = \overset{\displaystyle CH_3}{\underset{\displaystyle OH}{As}} - OH$$

Monosodium methanearsonate (MSMA): monosodium acid methanearsonate; the sodium salt of methanearsonic acid; CH_3AsO_3Na; an organic arsenical herbicide, also a naturally occurring compound;



$$O = \overset{\displaystyle CH_3}{\underset{\displaystyle ONa}{As}} - OH$$

Trimethylarsine gas (TMA): here arsenic has a valence of -3; $(CH_3)_3As$; a naturally occurring compound produced by organisms, especially fungi, from arsenate; toxic; volatile; has the odor of garlic;



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - As - CH_3 \end{array}$$

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Common Name: Picloram

Chemical Name: 4-amino-3,5,6-trichloropicolinic acid

Major Trade Names: Tordon; Amdon

Major Applications in Forestry: Used in virtually all geographic regions of the U.S. primarily in site preparation and occasionally in precommercial thinning and conifer release.

SUMMARY

The fate of picloram in the forest environment has been the subject of limited studies. Most of the available information on the fate of picloram in soil and water is the result of laboratory and/or field studies with agricultural systems.

Picloram is rapidly absorbed by plant roots and less rapidly by foliage. Once absorbed, it is readily translocated throughout the plant with a tendency for accumulation in new growth. It is very stable and remains largely intact within the plant, although small amounts degrade via decarboxylation, conjugate formation and other mechanisms.

Picloram is considered "moderately" to "highly" persistent in soils under conditions of normal application and may exist at phytotoxic levels for over one year. Reported half-lives vary from one to over 13 months. Persistence is generally shorter in soils with high organic matter content and adequate moisture such as may be present in forest soils, and in warm temperatures. Picloram degradation in soil occurs via microbial rather than chemical routes. Even under conditions highly favorable to microbial growth, however, amounts of picloram decomposed are small. Picloram undergoes photodecomposition on soil surfaces. Photodecomposition on soil occurs to the greatest extent under intense sunlight, and hence is not expected to be great in forest systems. Volatilization is not likely to be a major mechanism for the dissipation of picloram and its formulations from forest soils because of their low vapor pressures.

Picloram is considered a mobile herbicide and is reversibly adsorbed on soil particles. Adsorption is greatest in soils high in organic matter, and increases with decreasing pH, particularly in clay soils. Leaching occurs to the greatest extent in sandy, light-textured soils and soils poor in organic matter content. Picloram did not leach below the upper few inches of soil in a forest floor in the Pacific Northwest. Picloram formulation may affect its leaching. Studies have shown that the potassium salt of picloram is more readily leached than the triisopropanolamine salt.

Because of the water solubility of picloram and its salts and its leaching tendencies, runoff from treated areas can contain relatively high concentrations of picloram. Field monitoring studies conducted on three forest plots in Oregon and Washington treated with 0.5 to 1 lb/acre picloram indicated that runoff of picloram is most likely if heavy rainfall occurs soon (1-2 months) after application. Picloram rapidly degrades in water in sunlight.

Picloram is phytotoxic to numerous non-target plant species. It is very toxic to young pine seedlings. Several incidents of damage to non-target plants due to picloram spray drift have been reported. Certain species of plants have been injured as long as five years after application as a result of the persistence of picloram.

Picloram and its salts are low in toxicity to fish and other aquatic organisms. It has low toxicity to warm-blooded animals and to soil microorganisms. Limited studies on picloram and picloram plus 2,4-D have indicated low toxicities of these compounds to bees. Picloram is rapidly excreted by and does not bioaccumulate in mammals. Picloram in water is not accumulated in invertebrates or in food chains.

Recent studies have shown that certain picloram ester formulations may be more toxic to fish than picloram and its salts due to the presence of the toxic impurity 2-(3,4,5-6-tetrachloro-2-pyridyl)-guanidine.

1.0 INTRODUCTION

Picloram, discovered in 1963, is a non-selective, wide-spectrum herbicide which is widely used for control of woody plants and most annual and perennial broadleaf weeds (1,2). Major non-forest uses are in brush control along utility rights-of-way, for weed and brush control in pastures and rangeland, and broadleaf weed control in small grains (2). It is also registered for use in combination with 2,4,5-T on permanent rangeland and pasture in Texas, New Mexico, and Oklahoma (3,4).

Picloram alone and/or in combination with 2,4-D (as various "Tordon" formulations) is used in the forest industry in virtually all geographic regions of the U.S., primarily in site preparation and occasionally in precommercial thinning (5,6). Picloram is occasionally used in combination with 2,4-D for the control of woody vegetations for conifer release; topkills of 90 percent or better have been achieved in such applications (7,8). However, it is not recommended for conifer release for herbaceous weed control by broadcast application since it can severely damage young conifers (9,10,11).

Tables 1 and 2 show the usage of picloram formulations for site preparation (woody vegetation and kudzu control) and pine release in the Southeast in 1979, respectively. For comparison, use data for all other pesticides reportedly used in the Southeast are also provided. As indicated in the table, picloram formulations were used in the site preparation for woody vegetation control in over 51,500 acres, or 52.8 percent of the total acreage treated. For pine release, picloram formulations were applied to 78,510 acres, or 68.3 percent of the total acreage treated. Tordon 10K and Tordon 101 were used almost exclusively in site preparation for kudzu control.

A complete picture of the picloram usage in forestry is not available for other geographic regions of the country. Data for usage on public lands in the Pacific Northwest indicate that while picloram usage has been substantial in recent years, picloram is not one of the most widely used pesticides in that region of the country. Picloram usages by U.S. Bureau of Land Management (in Oregon) and by U.S. Forest Service in Regions 5 and 6 are presented in Tables 3, 4, and 5, respectively. Available data on the use of picloram formulations by the State of Minnesota, Department of Natural Resources, are presented in Table 6.

TABLE 1. FOREST HERBICIDE USAGE IN THE SOUTHEAST IN 1979 FOR SITE PREPARATION (12)

Woody Vegetation	Acreage	Amount	Method of Application
2,4-D Amine	30,000	12,093 gal	injection
Hexazinone (Gridball)	160	1,900 lb.	ground & aerial
Tordon 101	2,425	3,014 gal.	aerial
Tordon 101R	25,411	10,444 gal.	injection
Tordon 101 + 2,4-DP	9,660	13,702 gal. 16,641 gal	aerial
Tordon 101 R + 2,4-D Amine	11,581	17,515 gal. 17,185 gal	injection
Tordon 101 + Garlon 3A	2,300	2,300 gal 1,150 gal	aerial
Tordon 10K	160	4,080 lb	aerial
2,4-DP	1,262	691 gal	aerial
2,4-D + 2,4-DP	1,480	1,910 gal each	aerial
Weedone 64	5,250	2,620 gal	injection
Weedone 170	4,280 2,714	4,280 gal 72 gal	aerial injection
Paraquat	839	200 gal	aerial
Silvisar	4	4 gal	injection
Subtotal 97,526			
Kudzu			
Tordon 10K	2,350	54,420	ground
Tordon 101	1,578	1,537 gal	ground
Hexazinone (WP)	5	15 lb	ground
Subtotal 3,933			
TOTAL 101,459			

TABLE 2. FOREST HERBICIDES USAGE IN THE SOUTHEAST IN 1979 FOR PINE RELEASE (WOODY VEGETATION) (12)

Chemical	Acreage	Amount	Method of Application
Tordon 101 R + 2,4-D Amine	47,562	2,400 gal each	injection
Tordon 101 R	15,316	9,385 gal	injection
Tordon 101	15,632	2,585 gal	injection
Hexazinone (Gridball)	375	5,000 lb.	aerial & ground
2,4-D	4,775	1,925 gal	injection
2,4-DP	12,000	6,000 lb	ground
Weedone 170	2,714	72 gal	injection
Formula 40	9,000	?	injection
Dedweed 40	7,665	?	injection
TOTAL	115,009		

TABLE 3. PICLORAM APPLICATIONS IN STATE OF OREGON BY U.S. BUREAU OF LAND MANAGEMENT, FISCAL YEARS 1978 AND 1979 (13)

FY	Formulation	Target Pest/Purpose	Acres Treated	Pounds Used
1979	Picloram	Yellow Star Thistle Noxious Weed	800	200
	Tordon K and Verzon 20	Mixed hardwoods, site preparation	890	4,450
	Picloram	Biological, Yellow Star Thistle	10	2.5
1978	Picloram	Yellow Star Thistle	692	.73
	Picloram	Biological, Yellow Star Thistle	10	2.5

TABLE 4. PICLORAM APPLICATIONS IN U.S. FOREST SERVICE REGION 5, FISCAL YEARS 1975-1979 (13)

FY	Formulation	Target Pest/ Purpose	No. of Sites Treated	Acres Treated	Pounds Used	Application Method
1979	Picloram	Fuelbreak	192	-	328	aerial
		Fuelbreak	199	-	249	aerial
		Thinning	20	-	7.2	ground
		Noxious weed control	60.25	-	30.6	ground
1978	Picloram	Chapparal, conifers	129	-	846	-
1977	Tordon 10K	Fuelbreak	-	459	30,323	-
		Noxious weed control	-	23	9	-
1976	Picloram	Noxious weeds	85	-	70	-
		Fuelbreak	235	-	213	-

TABLE 5. PICLORAM APPLICATIONS IN U.S. FOREST SERVICE REGION 6, FISCAL YEARS 1975-1979 (13)

FY	Formulation	Target Pest/ Purpose	No. of Sites Treated	Pounds Used	Application Method
1979	Picloram	Vegetation thinning	353	12	Ground
	2,4-D + Picloram	Vegetation control/ site preparation	2,109	10,132	Aerial
	2,4-D + Picloram	Conifer release	42	198	Ground
	Picloram	Noxious weed control	477	148	Ground
	Tordon 10K	Vegetation control, powerline row	7	42	Ground
	Tordon 101	Vegetation control, powerline row	7	42	Ground
1978	Picloram	Site preparation	2,609	11,219	-
	Picloram	Release	903	77	-
	Picloram	Noxious weed control	229	389	-
	Picloram + 2,4-D	Noxious weed control	52	12	-
	Picloram	Right-of-way	171	685	-
1977	Picloram	Thinning	1	2.5	-
	Picloram	Site preparation	495	115.5	-
	Picloram	Site preparation	35	17.5	-
	Picloram	Site preparation	757	379	-
	Picloram	Release	1,069	50	-
	Picloram	Noxious weed control	1,701	22	-
	Picloram	Noxious weed control	129.2	295.9	-
	Tordon 22K	Noxious weed control	47	82.5	-
	Picloram	Road Right-of-way	9	36	-
	Picloram	Powerline Right-of-way	97	70	-
	Tordon 10K	Powerline Right-of-way	45	13	-
1975	Tordon 101	Timber management	7,545	908	-
	Tordon 101	Mistletoe control/ tree injection	412	46	-
	Tordon 10K	Poison oak	2	5	-
	Tordon 10K	Control of wood, plants near powerlines	40	60	-
	Tordon 101	Brush under powerlines	326	3,988	-

TABLE 6. TORDON 101 USAGE BY MINNESOTA DEPARTMENT OF NATURAL RESOURCES (14)

Administrative District	Target Pest or Purpose	Amount Used	Units Treated	Remarks
A) January 1 - June 30, 1980				
Lewiston Area	Release of black walnut	6.5 gal	721 acres	Miscellaneous hardwoods injected with hack and squirt method
Lewiston Area	Release of pine	20.75 gal	41 acres	Miscellaneous hardwoods injected with hack and squirt method
Red Wing District	Boxelder	1 gal	5 acres	Site preparation for walnut planting
Lake City District	Weed trees	7.5 gal	144 acres	Timber stand improvement
B) January 1 - June 30, 1979				
Region V	Weed trees	8 gal	41 acres	Winter application not 100% effective; injection method used
Region V	Boxelder, elm	25 lbs	5 acres	---
C) July - December, 1979				
Red Wing District	Boxelder, elm	19 gal	43 acres	---
Lake City District	Elm, boxelder	2 gal	10 acres	---
Lake City District	Miscellaneous hardwoods	1/2 gal	10 acres	---
Lewiston Area	Walnut TSI	1 gal	35 acres	Competing trees injected with 2 ml/diameter inch
Lewiston Area	Release of pine	15 gal	20 acres	Miscellaneous hardwoods injected with hack and squirt method. Cut stump type applications also used.
D) July 1 - December 31, 1978				
Lewiston Area	Release of black walnut	1 qt	3 acres	Killed competing hardwoods and pruned walnut

Picloram can be applied as: 1) a spray solution to foliage; 2) injected as a liquid formulation into tree or brush stems or applied as a cut surface treatment, or applied as pellets to the ground to be leached into the root zone by rainfall (15). Liquid formulations are applied aerially, or by means of ground equipment, knapsack equipment and tree injection. The granular formulation is applied by hand or with commercial granular applicators (1). Liquid formulations are usually aqueous solutions and are applied at rates of 2 oz to 3 lb/acre of picloram. Pellets are usually applied at a rate of 2 to 8 lb/acre (1). Tree injection rates are typically 1 ml/injection of Tordon 101 formulation (7). Applications are usually made from spring to 3 weeks before the first frost (5).

Picloram is a growth regulator, but its exact mode of action has not been established (16,17). It is absorbed by both roots and foliage, is translocated throughout the plant, and is accumulated in points of new growth (16,17).

Major forest weed species which are controlled by picloram include aspen, blackgum, brambles, buttonbush, Canada thistles, chokecherry, conifers, field bindweed, gallberry, hickory, juniper sp., kudzu, mulberry, redbud, sassafras and sourwood (17,18,19). Table 7 presents the relative susceptibility of a number of woody plants to foliage-applied sprays of picloram and picloram plus 2,4-D. Picloram is also effective in erradicating chamise, a chaparral species (21). A large number of deep-rooted perennial broadleaves such as bindweed, leafy spurge and larkspur are readily controlled with 2 pounds per acre of various Tordon formulations (22). Most established perennial grasses are not affected by rates of 1 to 2 pounds per acre (22).

Formulations of picloram commonly used in forestry, their active ingredients and inert carriers are presented in Table 8. Other available formulations for use in rangeland and cropland are listed in Table 9. A number of formulations which have previously been used in non-forest applications are no longer produced. These include: Tordon 2S Weedkiller (21.5 percent picloram as the potassium salt); Tordon 155 (10.3 percent picloram as the isooctyl ester plus 41.3 percent 2,4,5-T as the propylene glycol butyl ether ester); and Tordon 212 (10.1 percent picloram as triisopropanolamine salt plus 20.2 percent 2,4-D as triisopropanolamine salt) (23).

TABLE 7. SUSCEPTIBILITY OF VARIOUS WOODY PLANTS TO FOLIAGE-APPLIED SPRAYS OF PICLORAM AND PICLORAM PLUS 2,4-D* (20)

Common Name	Scientific Name	Picloram 2,4-D(1:4)	Picloram
Alder	*Alnus* ssp.	S	S
Ash	*Pyrus & Fraxinus* ssp.	I	I
Barberry, common	*Berberis vulgaris*	S	S
Basswood	*Tilia americana*	S	S
Beech	*Fagus* ssp.	S	S
Birch	*Betula* ssp.	S	S
Blackberry	*Rubus* ssp.	S	S
Broom, scotch	*Cytisus scoparius*	S	S
Buckthorn, European	*Rhamnus cathartica*	S	S
Caragana, common	*Caragana arborescens*	-	-
Cherry	*Prunus* ssp.	S	S
Cedar, Western	*Thuja plicata*	S	S
Cedar, yellow	*Chamaecyparis nootkatensis*	S	S
Currants	*Ribes* ssp.	S	S
Dogwood, red osier	*Cornus stolonifera*	S	S
Elderberry	*Sambucus* ssp.	S	S
Elm	*Ulmus* ssp.	S	S
Fir, balsam	*Abies amabalis*	S	S
Fir, Douglas	*Pseudotsuga taxifolia*	I	I
Gorse	*Ulex europaeus*	S	S
Hazel	*Corylus* ssp.	S	S
Hardhack	*Spiraea tomentosa*	S	S
Hawthorn	*Crataegus* ssp.	S	S
Hemlock, Western	*Tauga heterophylla*	S	S
Honeysuckle, bush	*Lonicera* ssp.	S	S
Hornbeam	*Ostrya virginiana*	S	S
Lilac	*Syringa vulgaris*	S	S
Locust, black	*Robinia pseudoacacia*	S	S
Maple, Manitoba	*Acer negundo*	S	S
Maple	*Acer* ssp.	S	S
Maple vine	*Acer circinatum*	I	I
Oak	*Quercus* ssp.	S	S
Pines	*Pinus*	S	S
Poison-ivy[b]	*Rhus radicans*	S	S
Poplar aspen	*Populus tremuloides*	S	S
Poplar, balsam	*Populus balsamifera*	S	S
Raspberry, wild	*Rubus* ssp.	S	S
Rose, wild	*Rosa* ssp.	S	S
Sagebrush, big	*Artemisia tridentata*	S	S
Salmonberry	*Ruus spectabilis*	S	I
Saskatoon	*Amelanchier alnifolia*	S	S
Snowberry (buckbrush)	*Symphoricarpus occidentalis*	S	I
Sumac	*Rhus* ssp.	S	S
Spruce (white,black)	*Pices* ssp.	S	S
Thimbleberry	*Rubus parviflorus*	S	S
Virginia creeper	*Parthenocissus quinquefolia*	S	S
Willows	*Salix* ssp.	S	S

*Susceptibility classification:

S = Susceptible-Woody plants which are usually killed by one application applied at the rate recommended.

I = Intermediate-Woody plants which usually require more than one application.

R = Resistant-Woody plants which are not killed by sprays applied at the recommended rate.

TABLE 8. PICLORAM FORMULATIONS FOR FORESTRY USE (4,20,23)

Formulation	Active Ingredients (Percent)	Active Ingredients (Weight)	Inert Carriers
Tordon 101[*]	10.2% picloram - triisopropanolamine salt. 39.6% 2,4-D - triisopropanolamine salt.	10 oz acid equivalent (a.i.)/ Imp. gal. triisopropanolamine salt. 40 oz a.i./Imp. gal. 2,4-D - triisopropanolamine salt.	Tordon 101 mixture also contains a glycol derivative sequestrant and glycol wetting agent along with alcohol and water.
Tordon 101R Mixture[†]	Appxoximately 5.1% picloram - triisopropanolamine salt. Approximately 20% 2,4-D - triisopropanolamine salt.	5 oz acid equivalent (a.i.)/ Imp. gal. triisopropanolamine salt. 20 oz a.i./Imp. gal. 2,4-D - triisopropanolamine salt.	Tordon 101R mixture also contains a glycol derivative sequestrant and glycol wetting agent along with alcohol and water.
Tordon 10K Pellets	11.6% picloram - potassium salt.	1.6 oz a.i./lb - potassium salt.	Clay.
Tordon K	24.0% picloram - potassium salt.	2.0 lb a.i./gal - potassium salt.	---

[*] Applied as a water spray (4).

[†] Applied via tree injection or cut surface treatment methods (4).

TABLE 9. PICLORAM FORMULATIONS FOR NON-FORESTRY USES (1,4,16,23)

	Picloram in Formulation			Other Herbicides in Formulation			
Trade Name of Product	% a.i.*	g/ liter	Deriva- tive†	Name†	%a.i.*	g/ liter	Deriva- tive†
Tordon 2K‡	2.3	-	K salt	-	-	-	-
Tordon 22K	24.9	-	K salt	-	-	-	-
Tordon 202 Mixture	1.4	15	TIPA salt	2,4-D	22.1	240	TIPA salt
Tordon 225E Mixture#	10.7	120	TEA salt	2,4,5-T	10.7	120	TEA salt
Tordon RTh	Same as Tordon 101R; see Table 8						

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* a.i. is acid equivalent (picloram, B_2O_3, 2,4-D, 2,4,5-T, and MCPA, respectively).

† K is potassium salt. TIPA is triisopropanolamine salt, and TEA is triethylamine salt.

‡ This formulation contains ammonium sulfate as the inert ingredient, and has replaced Tordon Beads which contained 2.3% picloram as the potassium salt, plus disodium tetraborate pentahydrate and disodium tetraborate decahydrate as the inert ingredients.

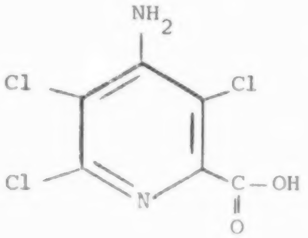
# Registered for use only in Texas, Oklahoma and New Mexico for mesquite control in rangeland and pastureland.

In addition to use with 2,4-D and 2,4,5-T, picloram has been shown to be efficacious when used in combination with triclopyr (24). In applications to 1/60-acre plots in central Louisiana, use of picloram at a rate of 1.0 lb a.i./acre in combination with triclopyr ester or 2,4,5-T ester at a rate of 3.0 lb a.i./acre resulted in over 90 percent topkill of mixed hardwood brush for two growing seasons. Picloram alone applied at a rate of 3.0 lb a.i./acre gave only 60 to 66 percent topkill under the same conditions (24).

Picloram is manufactured by the Dow Chemical Company. In addition to Tordon, it is also known by the trade name Amdon (2).

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The active ingredient of picloram is 4-amino-3,5,6-trichloropicolinic acid:



It is a white colorless crystalline substance which decomposes at 215°C before melting (16,25). Picloram is a monocarboxylic acid with a dissociation constant, pKa, of 3.6 (26). It is stable in both acidic and basic media, but may hydrolyze to the 6-hydroxy derivative in the presence of hot concentrated alkali (27).

Picloram is only very slightly soluble in water (430 mg/l), but its potassium and amine salts are highly water soluble (25). Solubility data for picloram and its salts at 25°C in various solvents are presented in Table 10.

Vapor pressure data for picloram, picloram methyl ester and picloram isooctyl ester (the active ingredient in Tordon 155) are shown in Table 11. Although no vapor pressure data are available for salts of picloram, the volatility of the salts are expected to be significantly less than the nonionic compounds shown in Table 11.

TABLE 10. SOLUBILITY (in mg/l) OF PICLORAM AND ITS POTASSIUM AND AMINE SALTS IN VARIOUS SOLVENTS (16,28)

Solvent	Picloram	Potassium Salt	Amine Salt
Acetone	19,800	100	---
Ethanol (2B-abs)	10,500	---	---
Isopropanol	5,500	240	---
Acetonitrile	1,600	---	---
Diethyl ether	1,200	---	---
Methylene chloride	600	---	---
Water	430	400,000	Highly soluble
Benzene	200	---	---
Carbon disulphide	50	---	---
Kerosene	10	100	---
Xylene	---	100	---

TABLE 11. VAPOR PRESSURE FOR PICLORAM AND TWO PICLORAM ESTERS (16,29)

Compound	Temperature (°C)	Vapor Pressure (mm of Hg)
Picloram	35 45	6.16×10^{-7} 1.07×10^{-6}
Picloram (methyl ester)	40	7.4×10^{-6}
Picloram (isooctyl ester)	40	5.88×10^{-6}

3.0 ENVIRONMENTAL FATE

Only a small body of environmental fate data have been published in connection with the use of picloram in forests. Most of the available data, which are included in the discussion in this section, are for non-forest applications.

3.1 UPTAKE AND METABOLISM BY PLANTS

Picloram is a growth regulator, but its exact mode of operation has not been established (16,17). Picloram is rapidly absorbed by plant roots and less rapidly by foliage (17,20,22). Rapid uptake of picloram by roots from nutrient solutions has been demonstrated in a number of studies using green ash (Fraxinus pennsylvania marsh), sweet gum (Liquidombar styracflua L.) and silver maple (Acer saccharinum L.) seedlings (30); huisache (Acacia farnesiana L. wild) and honey mesquite (Prosopis juliflora) (31); and oats, soybeans (32), and peas (33). Rapid uptake of picloram by roots from soil has also been demonstrated with young huisache (34) and leafy spurge plants (35). Picloram sprayed on the leaves of yaupon (Slex vomitoria, Ait) at 4.4 kg/ha resulted in only 2 percent absorption after 72 hours (36). In studies on bean seedlings, 7 days were required before 90 percent of the foliage applied picloram was absorbed.

Once absorbed, picloram is readily translocated throughout the plant with a tendency for accumulation in new growth (17,22). Relatively little is known about the metabolism and fate of picloram and its derivatives or degradation products in plants. Most studies have shown that picloran itself is very stable and remains largely intact within the plant (37,38). Redemann, et al. (39) reported that the major compounds present in extracts of 84-day-old wheat plants treated at 1.0 kg/ha were: the parent compound, 83 percent; oxalic acid, 8 percent; 4-amino-2,3,5-trichloropyridine, 4 percent; and 4-amino-3,5-dichloro-6-hydroxypicolinic acid, 5 percent. Decarboxylation also is suggested as a possible degradation pathway (37). In a study using cotton, however, the rate of decarboxylation was very slow, indicating that it was not an important mechanism for picloram metabolism in plants. Residue analysis in this study indicated the presence of no other compound besides picloram. Picloram has also been reported to form conjugates with various plant constituents including proteins (37,38,39).

3.2 FATE IN SOIL

Processes which affect the fate of picloram in soil are volatilization, photodecomposition, adsorption and leaching, runoff, and chemical and microbial degradation.

Volatilization is not expected to be a major mechanism for dissipation of picloram from soil because of the low vapor pressure of picloram and its formulations (see Section 2). This has been indicated in 2 laboratory studies in which vapor losses from the potassium salt of picloram from open petri dishes maintained at 55 to 60°C were less than 5 percent over a one-week period (40,34). The contributions of the remaining processes to the fate of picloram in soil are described below.

3.2.1 Photodecomposition

Picloram undergoes photodecomposition on the soil surface and on the surface of vegetation due to the action of uv radiation in sunlight (1,41, 42). Photodecomposition occurs to the greatest extent under intense sunlight (42).

Laboratory studies by Merkle, et al. (40) indicated that 60 percent of picloram, when spread evenly on a glass surface, was degraded by uv light within 48 hours, whereas 35 percent was degraded by sunlight in the same time period. After one week's exposure, over 90 percent was degraded by uv light and 65 percent by sunlight. Degradation from soil surfaces was slower than from glass; only 15 percent of the applied picloram was degraded after one week in sunlight. In studies by Bovey and Scifres (43), salt forms of picloram were found to be less subject to photodecomposition than ester forms.

The mechanism and products of picloram photodegradation in soil have not been fully investigated, although there are recent indications that cleavage of the pyridine ring occurs (1).

3.2.2 Adsorption and Leaching

Picloram is reversibly adsorbed on soil particles and is generally considered a mobile herbicide (3). The extent of adsorption and hence potential for mobility and leaching is dependent on soil type (primarily organic matter content), pH, application rate, the amount of water applied (rainfall) and the picloram formulation. Soil organic matter is the principal parameter responsible for adsorption and adsorption can be substantial in forest litter having high organic matter content (3,44). It has been postulated that soil humic substances retain picloram initially via surface adsorption and subsequently via adsorption/occlusion within the internal structures (45).

Picloram adsorption on soils generally increases with decreasing pH, particularly in clay soils, and is minimimal in neutral and alkaline soil types (20,46,47,48,49). Picloram is also strongly adsorbed by hydrated oxides of aluminum and iron (50) and this accounts for some adsorption which occurs in clay soils.

Consistent with the adsorption properties of various soil types, leaching of picloram occurs to the greatest extent in sandy, light-textured soils and in soils poor in organic matter (1,3,20). A number of studies have shown that picloram remains in the upper 20-30 cm of soil for most soil types except sandy soils (3). In a study of the leaching of picloram in connection with its use in powerline rights-of-way weed control in the Pacific Northwest, no picloram was leached below 30 cm in the soil, and very little leached below 15 cm (6). In a separate study essentially no picloram leached below the upper inches of soil in a forest floor (6). Norris (51) reported that picloram applied to a southern Oregon hillside pasture was largely confined to the surface 6 inches of soil. For most soil types, the extent of picloram leaching in soil is affected by the amount of water (rainfall) applied and the picloram application rate.

The extent of picloram leaching is also a function of total amount of water and the rate of picloram applied. In a recent study by Grover (52), it was shown that increasing the amount of water applied from 0.25 to 2.5 cm enhanced the movement of picloram in a heavy clay soil, but had no effect on a sandy loam. There was little or no difference in movement when the herbicide was applied at 0.2 or 2.0 kg/ha. In a sandy loam, picloram leached to a greater depth when the soil was initially dry rather than wet. Field studies have demonstrated that at low rates of application, picloram rarely moves downward beyond the upper 30 cm of soil, particularly in semi-arid regions (53,54,55). At high rates of application, picloram readily leaches downward to over 100 cm, even in a relatively dry area (35). The results of various field studies reflecting the effects of soil type, pH, rainfall and application rate on picloram leaching are summarized in Table 12.

TABLE 12. SUMMARY OF SOIL PROFILES OBTAINED IN VARIOUS FIELD STUDIES ON LEACHING BEHAVIOR OF PICLORAM (20)

<table>
<tr><th rowspan="3">Locality</th><th rowspan="3">Soil type</th><th rowspan="3">pH</th><th rowspan="3">Organic matter (%)</th><th rowspan="3">Rain-fall (cm)</th><th rowspan="3">Appli. rate (kg/ha)</th><th rowspan="3">Sampl. interv. (days)</th><th colspan="10">Picloram recovery at indicated depths (cm)</th></tr>
<tr><th>0-2.5</th><th>0-5</th><th>0-15</th><th>15-30</th><th>30-45</th><th>45-60</th><th>60-75</th><th>75-90</th><th>90-105</th><th>105-120</th></tr>
<tr><th colspan="10">(ppb)</th></tr>
<tr><td>Texas</td><td>fine s.l.</td><td>5.0-6.0</td><td>-</td><td>15.0</td><td>8.96</td><td>42</td><td>60</td><td>-</td><td>330</td><td>180</td><td colspan="2">160</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Texas</td><td>gravelly s.l.</td><td>5.5</td><td>-</td><td>8.6</td><td>8.96</td><td>84</td><td>60</td><td>-</td><td>120</td><td>60</td><td colspan="2">50</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Ohio</td><td>silty c.</td><td>6.0-6.6</td><td>4.4-1.1</td><td>40.1</td><td>4.48</td><td>280</td><td>-</td><td>-</td><td>400</td><td>368</td><td>136</td><td>39</td><td>18</td><td>14</td><td>-</td><td>-</td></tr>
<tr><td>Ohio</td><td>silt l.</td><td>6.1-5.8</td><td>2.9-1.0</td><td>63.3</td><td>4.48</td><td>245</td><td>-</td><td>-</td><td>232</td><td>80</td><td>114</td><td>210</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Ohio</td><td>silt l.</td><td>6.0-7.1</td><td>3.9-0.9</td><td>69.3</td><td>4.48</td><td>270</td><td>-</td><td>-</td><td>220</td><td>146</td><td>184</td><td>104</td><td>78</td><td>32</td><td>-</td><td>-</td></tr>
<tr><td>Saskatchewan</td><td>c. l.</td><td>7.2</td><td>4.0</td><td>-</td><td>4.48</td><td>350</td><td colspan="2">900</td><td>750</td><td>424</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Saskatchewan</td><td>l.</td><td>5.7</td><td>4.0</td><td>-</td><td>0.56</td><td>435</td><td colspan="2">38</td><td>38</td><td>37</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Alberta</td><td>l.</td><td>8.0</td><td>11.0</td><td>-</td><td>1.12</td><td>330</td><td colspan="4">I—83—I—99—I—38—I—37—I</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Alberta</td><td>l.</td><td>5.7</td><td>11.0</td><td>-</td><td>0.28</td><td>435</td><td colspan="4">I—49—I—16—I—0—I—0—I</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Texas</td><td>c.l.</td><td>-</td><td>-</td><td>35.6</td><td>10.08</td><td>180</td><td>-</td><td>-</td><td>220</td><td>210</td><td colspan="2">80</td><td colspan="2">10</td><td colspan="2">0</td></tr>
<tr><td>Texas</td><td>s.</td><td>-</td><td>-</td><td>33.0</td><td>10.08</td><td>180</td><td>-</td><td>-</td><td>30</td><td>10</td><td colspan="2">50</td><td colspan="2">60</td><td colspan="2">60</td></tr>
<tr><td>Nebraska</td><td>silty c.l.</td><td>6.6</td><td>4.7</td><td>137.8</td><td>2.24</td><td>~2-yr</td><td colspan="4">2</td><td colspan="2">2</td><td colspan="2">25</td><td>-</td><td>-</td></tr>
<tr><td>Nebraska</td><td>silty c.l.</td><td>5.6</td><td>2.7</td><td>69.6</td><td>1.12</td><td>~1-yr</td><td colspan="4">17</td><td colspan="2">2</td><td colspan="2">2</td><td>-</td><td>-</td></tr>
<tr><td>Nebraska</td><td>fine s.l.</td><td>7.5</td><td>1.8</td><td>47.6</td><td>2.24</td><td>~1-yr</td><td colspan="4">22</td><td colspan="2">32</td><td colspan="2">28</td><td>-</td><td>-</td></tr>
<tr><td>Nebraska</td><td>silty c.l.</td><td>6.8</td><td>4.3</td><td>59.9</td><td>2.24</td><td>~1-yr</td><td colspan="4">20</td><td colspan="2">0</td><td colspan="2">1</td><td>-</td><td>-</td></tr>
<tr><td>Puerto Rico</td><td>c.</td><td>-</td><td>-</td><td>124.5</td><td>10.08</td><td>180</td><td>-</td><td>-</td><td>883</td><td>612</td><td>-</td><td colspan="2">215</td><td colspan="2">62</td><td>109</td></tr>
<tr><td>Puerto Rico</td><td>s.</td><td>-</td><td>-</td><td>53.3</td><td>10.08</td><td>180</td><td>-</td><td>-</td><td>0</td><td>0</td><td>-</td><td colspan="2">0</td><td colspan="2">0</td><td>-</td></tr>
<tr><td>Texas</td><td>s.l.</td><td>7.1</td><td>1.5</td><td>2.5</td><td>0.28</td><td>28</td><td>113</td><td>-</td><td>31</td><td colspan="3">0</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Texas</td><td>l.s.</td><td>7.6</td><td>1.2</td><td>-</td><td>0.28</td><td>36</td><td>38</td><td>-</td><td>8</td><td colspan="3">0</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>Texas</td><td>fine s.l.</td><td>-</td><td>-</td><td>8.9</td><td>1.12</td><td>30</td><td>-</td><td>-</td><td>93</td><td>18</td><td>-</td><td>2</td><td>-</td><td>1</td><td>-</td><td>2</td></tr>
<tr><td>Kansas</td><td>s.c.l.</td><td>-</td><td>2.2</td><td>-</td><td>3.36</td><td>3-yr</td><td colspan="3">229</td><td>279</td><td>278</td><td colspan="2">31</td><td colspan="3">43</td></tr>
<tr><td>Saskatchewan</td><td>heavy c.</td><td>7.7</td><td>4.1</td><td>64.3</td><td>4.48</td><td>~2-yr</td><td>-</td><td>162</td><td>143</td><td>78</td><td colspan="2">111</td><td colspan="2">157</td><td colspan="2">32</td></tr>
<tr><td>Saskatchewan</td><td>sandy l.</td><td>7.5</td><td>1.8</td><td>~64.0</td><td>4.48</td><td>~2-yr</td><td>-</td><td>233</td><td>156</td><td>33</td><td colspan="2">118</td><td colspan="2">100</td><td colspan="2">28</td></tr>
<tr><td>Manitoba</td><td>c.</td><td>6.8-7.4</td><td>8.8-2.6</td><td>73.5</td><td>0.70</td><td>439</td><td>-</td><td>-</td><td>70</td><td>30</td><td colspan="2">6</td><td>-</td><td>-</td><td>-</td><td>—</td></tr>
</table>

s. = sandy; l. = loam; c. = clay
Dashes (-) indicate no samples were taken.

The type of picloram formulation used may or may not affect its leaching in soil. Hunter and Stobbe (55) reported that the potassium salt of picloram leached more readily than the triisopropanolamine salt. In a leaching study conducted by Bovey and Scifres (43), however, the leaching patterns of picloram salts and esters were found to be similar. Where esters were used, the unhydrolyzed esters were found in the top 5 cm of soil; only the acid form was found below 5 cm. It was not possible to distinguish between the acid and salt formulations.

3.2.3 Runoff

Because of the water solubility of picloram (especially its salts) and its leaching tendencies, runoff from areas treated with picloram can contain relatively high concentrations of picloram. Based on field monitoring data for three forest plots in Oregon and Washington treated with 0.5 to 1 lb/acre of picloram, in which maximum picloram concentrations of 20 to 78 ppb occurred in runoff during storm events, Norris (56) concluded that runoff of picloram can occur after the first heavy autumn rains if application is in mid or late summer and that the greatest potential for runoff exists when the storms are sufficiently intense to cause overland flow rather than infiltration. In a separate study, losses of picloram from a Tordon 101-sprayed podsol in a Great Lakes forest clearcut were measured for 13 months following spraying (57). A rainfall occurring less than 24 hours after spraying released only a very minute amount of picloram and only less than 1 percent of the applied picloram was lost as a result of seven runoff events which occurred during the monitoring period.

Based on a large number of non-forest and several forest field studies, it is generally held that a potential exists for high concentrations of picloram in runoff if heavy rainfall occurs soon after application (58). Bovey, et al. (34) found that maximum concentrations of picloram were 400 to 800 ppb in surface runoff water if heavy rainfall occurred immediately after spraying a 1:1 mixture of triethylamine salts at 1.12 kg/ha on grassland watersheds. However, if major storms occurred within 1 month after application, picloram concentrations were less than 5 ppb. Picloram residues in drainage from a forest plot in Ontario, Canada, sprayed with 0.9 kg/ha were 38 ppb one day after application, 26 ppb after 7 weeks, and 1 ppb after one year (60).

The fact that only a very small percentage of the applied picloram from the treated areas would enter the runoff has been demonstrated in a relatively large number of field studies in non-forest applications. These studies, summarized in Table 13, indicate maximum picloram losses of less than 3 percent. These studies have also shown that concentration of picloram in runoff water generally decreases with time, and also with time-lapse from application to the first rainfall. In one of the studies (61) where picloram was applied at a rate of 1.12 kg/ha on an 8-ha site, about 10 ppb of picloram was present in runoff water adjacent to plots 10-12 weeks after application. Water sampled 8 days after application at a distance of 1.2 km from the plots had less than 1 ppb of picloram. With heavy rainfall 2 days after application, high amounts of picloram (26.2-89.7 ppb) occurred in runoff waters in areas adjacent to the plots. Eight months after treatment, the runoff water contained less than 1 ppb at a distance of 1.6 km from the plots. Application of picloram pellets to riparian vegetation at a rate of 9.0 kg/ha on 4.5 percent of a forested watershed in Arizona produced a maximum stream concentration of 370 ppb after one storm of 72 mm (59). In the following 2 months, ten storm events totalling 103 mm of rainfall produced a maximum picloram concentration of 52 ppb. Five successive storms totalling 56 cm of rainfall over the next week resulted in a maximum picloram concentration of 350 ppb (59). In another study by Trichell (62,63), approximately 5 percent of the picloram applied to small plots was lost in runoff water when a simulated rainfall of 1 inch per hour was applied 24 hours after treatment.

The concentration of picloram in runoff water is also affected by slope and soil compaction. Studies by Scifres (53) and Trichell (64) have demonstrated that picloram concentration in runoff decreases more as the runoff passes over untreated compacted soil (especially sod) than over uncompacted (fallow) soil. The effects of slope and rate of application on the concentration of picloram in runoff passing over untreated sod is shown in Table 14. As indicated by the data, higher concentrations of picloram are associated with higher slopes and in the lower half of the slope.

The runoff potential using picloram pellets has been evaluated and, in one field study, compared with that using liquid sprays. Bovey, et al. (65) demonstrated that loss of the potassium salt of picloram from grassland watersheds in surface runoff water was similar whether the picloram was

TABLE 13. RESIDUES OF PICLORAM IN SURFACE RUNOFF WATERS AT DIFFERENT TIME INTERVALS (DAYS IN BRACKETS) AFTER APPLICATION OF PICLORAM AT VARYING RATES (20)

Type of area treated	Rate applied	Picloram residues in water at different times after application*		
	(kg/ha)		(μg/l)	
Watersheds (Texas)	1.12	9-168 (4)	<5 (90)	0 (300)
Watersheds (Arizona)	1.90	-	-	<100 (365)
Watersheds (Arizona)	10.40	370 (10)	Trace(90)	0 (365)
Semi-arid rangeland (Texas)	0.28	17 (10)	<1 (30)	-
Semi-arid rangeland (Texas)	1.12	26-90 (2)	10 (70)	<1 (365)
Semi-arid watershed (Texas)	0.28-2.24	-	-	19 (365)
Sub-humid watershed (Texas)	0.28-2.24	184 (7)	0 (180)	-
Grassland (Texas)	1.12	55-184 (14)	2-29 (42)	<1 (365)
Sod (Texas)	1.12-2.24	2170 (1)	27 (120)	-
Fallow (Texas)	1.12-2.24	650 (1)	15 (120)	-

* All sampling areas located immediately adjacent to treated plots.

TABLE 14. EFFECT OF SLOPE, RATE OF APPLICATION, AND MOVEMENT OVER UNTREATED SOD ON THE CONCENTRATION OF PICLORAM IN RUNOFF WATERS (64)

Rate[*] (lb/A)	Slope (%)	Portion of plot treated	Picloram in runoff water[†] (ppm)	Picloram runoff (% of applied)
2	8	upper half	2.1	1.6
1	8	entire	3.8	5.5
2	3	upper half	1.3	0.9
1	3	entire	2.0	2.8

[*] Picloram applied as potassium salt in water (400 g/A).

[†] Simulated rainfall 0.5 in/hr 24 hours after herbicide application.

applied as an aqueous spray or pellet. Davis, et al. (66) applied pelleted picloram (10 percent) at 10.4 kg/ha to a 0.9-ha drainage area in an 18.8-ha watershed in central Arizona. The highest concentrations of picloram in runoff collected 7 days after application and a 6.4-cm rainfall was 0.37 ppm. Only trace amounts of picloram were present after 3 months and picloram was not detectable after one year.

Burnett, at al. (67) measured and compared picloram concentrations in runoff from large watersheds in Texas to which either a picloram spray or picloram formulated in starch xanthate granules were applied. The results indicated that picloram was slowly released from the starch granules over a period of several months, and that application of the granule formulation eliminated the initial large concentration of picloram in runoff water which occurred with the spray. Immediately after application at a rate of 2 kg/ha, picloram concentrations in the runoff water averaged 112 ppb and 6 ppb, respectively, on watersheds treated with the conventional spray and with starch xanthate granules. Picloram concentrations from the sprayed watershed later decreased to 0.1 ppb, while concentrations from the watershed treated with the starch granule formulation increased for several weeks, remained at 20 ppb for 14 weeks, and then decreased to 4 ppb after 8 months. Cumulative amounts of picloram lost in nine rainfall events represented 2.5 percent of that applied as a spray at 2 kg/ha, and 1.5 percent of the herbicide applied as the starch xanthate granules at 2 and 4 kg/ha. Picloram concentrations in the upper 15 cm of soil were also greater on plots treated with the slow release granules than with the spray.

3.2.4 Persistence and Degradation

Picloram is considered "moderately" to "highly" persistent in soils under conditions of normal application and may exist at phytotoxic levels for over one year (68). Reported half-lives vary from one to over 13 months (15,3). Persistence in soil is affected principally by soil type, moisture and temperature. Persistence is generally shorter in soils with high organic matter content. In forest soils it has been shown that picloram degrades within one year after application (9,17). Field studies conducted in the Pacific Northwest have indicated that Douglas-fir can be planted within 8 months to one year after application of up to 1 lb picloram plus 4 lb a.i. of 2,4-D/acre (69). In a study of the persistence of picloram on powerline rights-of-way in the Pacific Northwest, Norris (70) found that damaging concentrations of picloram were seldom present more than 12 months after application.

Picloram is very persistent in clay and sandy loam soils having low organic matter content, and in cold, dry climates (71). In a field study in which picloram was applied to fallow Somerset sandy loam soil in the cold, dry climate of Nova Scotia, it was found that crops susceptible to low concentrations of picloram were damaged even after 1,055 days after application (72). Keys and Friesen (53) reported that residues of picloram applied at 0.6 kg/ha in the fall declined to about 10 percent after 24 months and to less than 6 percent after 35 months. Residues from picloram application at 3.24 kg/ha to patches of persistent weeds in central Alberta, Canada, croplands were found to be sufficiently high to delay germination of sensitive crops even in the fifth year after treatment (73). Studies by Fryer, et al. (74) have shown that 5 to 6 percent of picloram applied at 1.68 hg a.i./acre to test plots of sandy loam soil in England was recoverable one year after application, and that this residue degraded slowly over the following 3 years to a level of 0.5 percent.

Additional studies by Hunter and Stobbe (55) indicated that dissipation of picloram was very slow under conditions of low soil moisture, with about 35 percent remaining after 2 years following application of 0.35 kg/ha picloram. Other field investigations have demonstrated that degradation of picloram is more rapid in warm humid clinates than in colder drier ones, especially in light-textured sandy soils (40,55,75). Picloram persistence also decreases with decreasing pH (26) and in the presence of plant roots (37).

The kinetics of picloram degradation has been studied and can best be described as being half to first order under practical application rates (3). Using a half order reaction kinetics model, Hamaker, et al. (76) calculated rates of picloram loss in soil samples collected from 18 states and two Canadian provinces (Table 15). The estimated rate constants, $k_{\frac{1}{2}}$, varied from 0.12 for Saskatchewan to 0.79 for Texas soils, and were highly correlated with the observed temperatures, with the rates being faster at higher temperatures.

Picloram degradation in soil occurs via microbial rather than chemical routes (77). (There is no breakdown of picloram when it is incubated in sterile soil at room temperature.) (26,52). Rates of microbial degradation increase under conditions which favor microbial growth, e.g., adequate moisture, warm temperature, adequate organic matter content, etc. However, even under the most favorable conditions, amounts of picloram decomposed are small (16), and picloram is considered not a good energy source for microorganisms but is co-metabolized with other energy sources. In studies by Meikle, et al. (37), only 4 percent of picloram was degraded in 15 days by plant-root and rhyzosphere microorganisms. Youngson, et al. (26) found that breakdown of picloram in nutrient cultures containing many different types of bacteria and fungi was only 0.24 to 1.21 percent. Naik, et al. (78) reported persistence of picloram in microbial cultures for more than 275 days.

The exact mechanism of picloram degradation in soil is not fully known and may vary with the organisms. Degradation by most microorganisms is believed to involve both decarboxylation of the ring carboxylic acid group and ring cleavage. Laboratory studies have shown that ring-labelled carbons in

TABLE 15. OBSERVED HALF-ORDER CONSTANTS ($k_{\frac{1}{2}}$)* FOR VARIOUS PROVINCES AND STATES OF CANADA AND UNITED STATES (76)

State or Province	Number of Soil Profiles Analyzed	Average $k_{\frac{1}{2}}$	90% Confidence Limits For Half-order Constants
Alberta	2	0.40	†
California	33	0.27	0.05
Colorado	4	0.25	0.13
Idaho	11	0.47	0.12
Illinois	3	0.62	†
Kansas	3	0.41	†
Michigan	7	0.17	0.05
Minnesota	6	0.19	0.11
Montana	34	0.22	0.03
Nebraska	2	0.19	†
Nevada	2	0.67	†
New Mexico	2	0.57	†
North Dakota	8	0.37	0.05
Oregon	4	0.21	0.04
Saskatchewan	6	0.12	0.05
South Dakota	11	0.37	0.20
Texas	46	0.79	0.12
Washington	22	0.40	0.09

*/ $k_{\frac{1}{2}} = \frac{2[\sqrt{c_o} - \sqrt{c}]}{t}$ where c_o = rate of application of the herbicide in ounces/acre (initial concentration)

c = final concentration of the herbicide in the soil at time (final concentration)

t = interval between treatment and analysis in months.

$k_{\frac{1}{2}}$ = half-order constant in [ounces per acre]$^{\frac{1}{2}}$ per month.

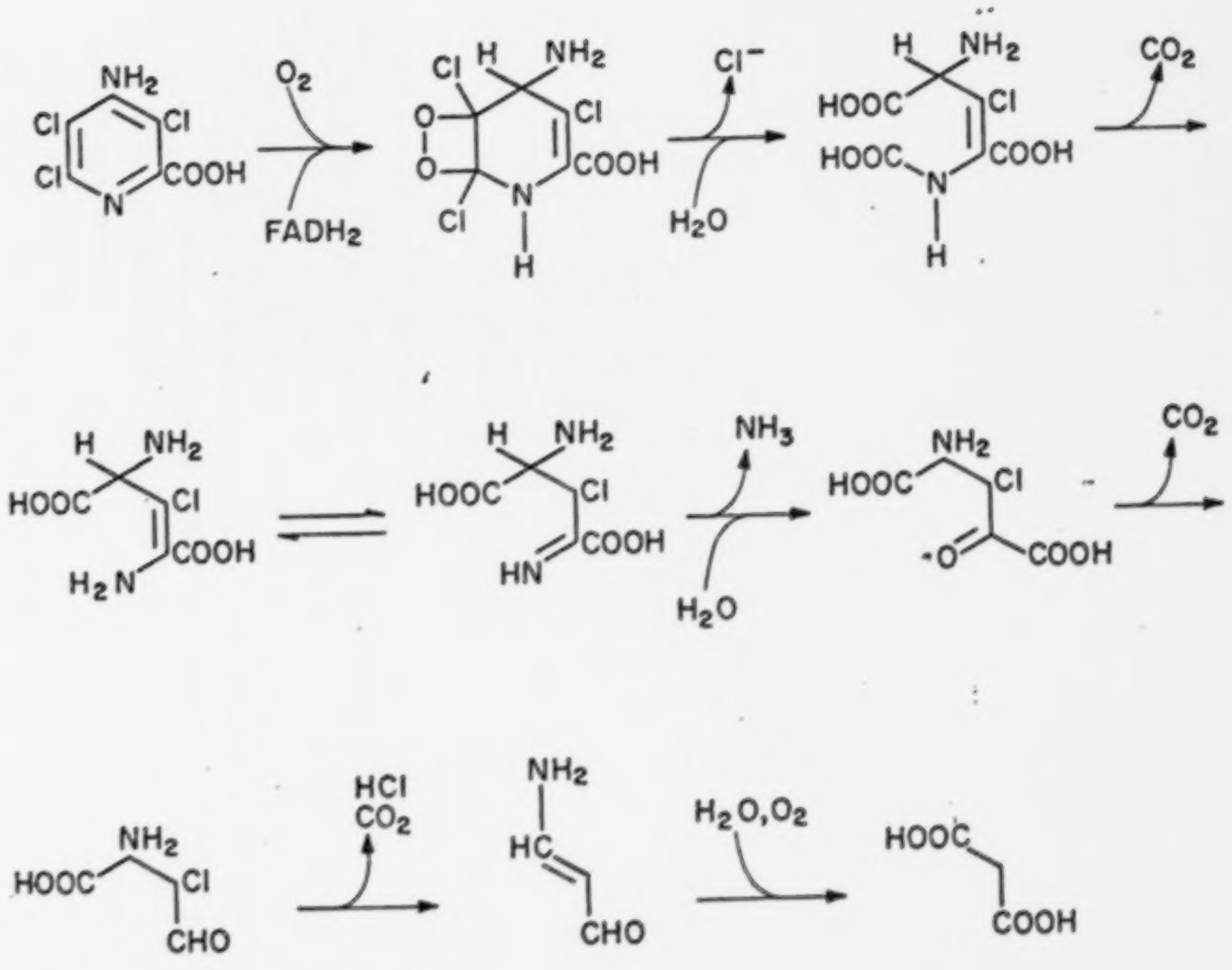
†/ 90% Confidence limits not estimated for fewer than four profiles in a state.

picloram are emitted as CO_2 at almost the same rate as carboxyl-labelled carbon, indicating that the degradation mechanism involves both ring cleavage and decarboxylation (79). A reaction sequence for the microbial decomposition of picloram involving both ring cleavage and decarboxylation was recently proposed by Meikle, et al. (80) and is presented in Figure 1. Additional degradation products which have been identified are 4-amino-2,3,5-trichloropyridine and 6-hydroxy-3,5-dichloro-4-aminopicolinic acid. Rieck (81) found that Trichoderma growth on broth media containing picloram resulted in the formation of 4-amino-2,3,5-trichloropyridine, the decarboxylated molecule, and that this metabolite was readily further assimilated by the fungus via ring cleavage reactions. The 6-hydroxy-3,5-dichloro-4-aminopicolinic acid reportedly is formed in only very small quantities (82,83).

The fate of picloram in bodies of water in forest areas treated with picloram has not been investigated. In an area in which 67 percent of a watershed was sprayed in August, residues up to 0.078 ppm were detected in nearby streams after an initial one-inch storm (84). A rapid decrease in the residue was observed subsequently, probably due to dilution and for degradation.

Picloram is not readily degraded by chemical and microbial routes in water. It is, however, readily degraded by uv light and sunlight. Photodegradation is the major degradation route for picloram in water (3,20,62). Laboratory studies have indicated a photolysis half-life varying from as little as 5 days in one-inch deep containers to as much as 60 days in noncirculating 12-foot deep containers (85). Hall, et al. (86) investigated picloram photolysis in basic aqueous solutions under uv light and sunlight. Approximately 20 percent of the picloram was degraded by 48-hour exposure to uv light, with slower and more variable degradation under sunlight.

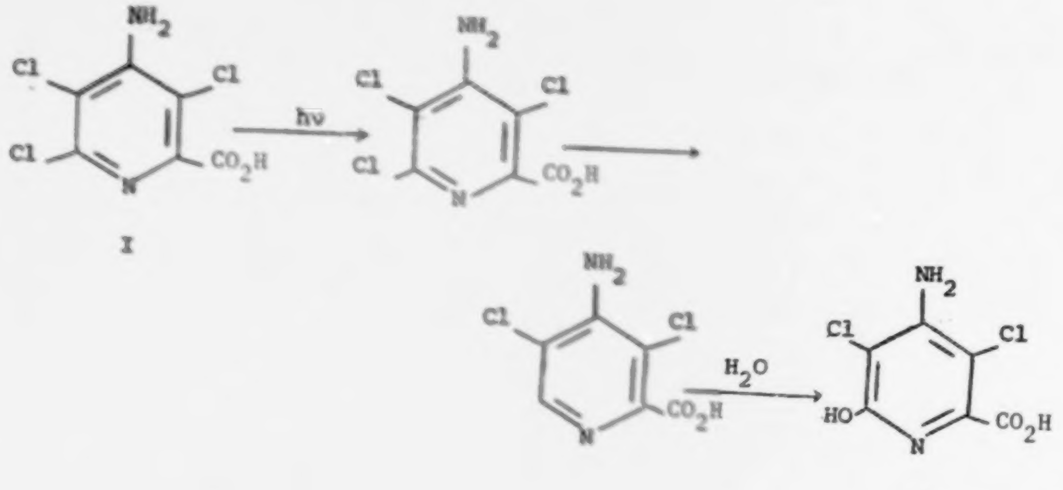
Research by Hedlund and Youngson (87) indicated that photolysis by sunlight of picloram in aqueous solutions followed pseudo-first order kinetics for concentrations up to 4.14×10^{-4}M and in circulating solutions as deep as 3.64 meters. Hazy sunlight and water impurities had only a small effect on the rate of photolysis in the systems studied. Studies by Michel, et al. (88) have shown that photolysis of picloram by uv light also follows pseudo-first order kinetics.



O2
FADH2
Cl⁻
H2O
CO2
NH3
H2O
CO2
HCl
CO2
H2O,O2

Figure 1. Proposed Mechanism for Microbial Decomposition of Picloram in Soil (80)

Numerous studies have been conducted to elucidate the mechanism of picloram photodegradation in water. The results indicate that picloram degradation may follow several pathways, resulting in different initial products (see Figure 2) which are further degraded. Studies by Hall, et al. (89) and Mosier and Guenzi (90) have shown that a free radical mechanism is likely to be involved in the formation of certain of the initial products. A possible sequence of reactions for photolysis of picloram to form initial product II (Figure 2) is as follows (90):



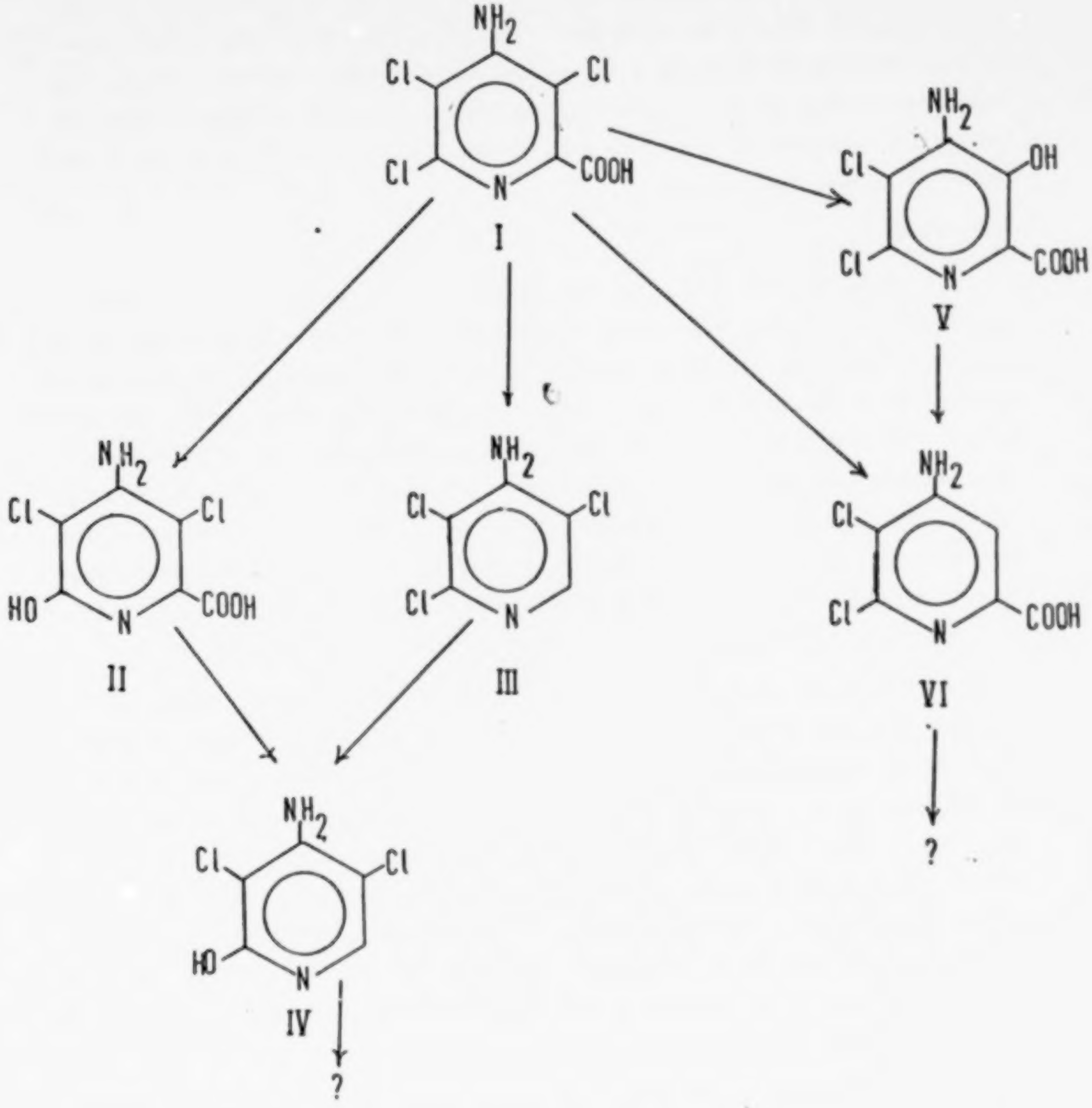
I

II

4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

4.1 PLANTS

As noted in Section 1.0, picloram is not recommended for conifer release by broadcast application since it can cause damage to young conifers. Wu, et al. (91) found that picloram was very toxic to young pine seedlings. At 50 mg/l applied as nutrient solution, picloram inhibited both root and shoot growth. Ryker (11) found that picloram used alone or in combination with 2,4-D damaged 2-year old conifer seedlings. In addition, several incidents of damage to non-target plants due to picloram spray drift have been reported. In one incident in southern Canada, trees 50 meters from a treated area were killed (20). In other incidents in Minnesota, drift of picloram from roadside spraying caused injury to nearby corn and soybean fields (92).



I. 4-amino-3,5,6-trichloropicolinic acid
II. 4-amino-3,5-dichloro-6-hydroxy-picolinic acid
III. 4-amino-2,3,5-trichloropyridine
IV. 4-amino-3,5-dichloro-6-hydroxy-pyridine
V. 3-hydroxy-4-amino-5,6-dichloro-2-picolinic acid
VI. 4-amino-5,6-dichloro-2-picolinic acid

Figure 2. Alternative Pathways for the Photodegradation of Picloram (20)

Because of its persistence in soil, phytotoxic levels of picloram may remain in soil long after treatment. Certain species of plants have been injured as long as five years after application (20). Gesnik, et al. (93) found that picloram plus 2,4-D (0.6 kg/ha + 2.2 kg/ha) applied to Wyoming rangeland resulted in injury to certain desirable perennial grasses up to 2 years following application.

4.2 FISH

Picloram and its salts are low in toxicity to fish and other aquatic species (3,94). LC_{50} values for various species of fish to picloram and its salts are shown in Tables 16 and 17. The median tolerance limits in ppm of Tordon 101 to various fish are: fathead minnow, 64; brook trout, 240; brown trout, 250; rainbow trout, 150; and green sunfish, 150. In a laboratory study using concentrations of picloram simulating field concentrations in runoff waters and streams, Woodward (95) found that picloram increased fry mortality in cutthroat trout (Salmo clarki) in concentrations greater than 1,300 μg/l and reduced fry growth in concentrations above 610 μg/l. Picloram had no adverse effects on fry concentrations below 290 μg/l.

In a study conducted by Butler (96), shrimp and oysters exhibited no effects when exposed to picloram at 1.0 ppm for 48 and 96 hours, respectively. Other studies by Butler demonstrated that mollusks were not susceptible to picloram up to a dose of 380 ppm, but a dose of 530 ppm resulted in 100 percent mortality of the mollusks (97). The estimated LC_{50} for stonefly nymphs (Ptesnarye californica) exposed for 27 hours to picloram was 120 ppm (98). The 48-hour LC_{50} for amphipods (Gammarus lacustris) was 48,000 ppm (99). Daphnia exposed to 380 ppm of picloram for 24 hours did not show any ill effects, but when exposed to 530 ppm, 95 percent of the Daphnia did not survive (100,101).

In a food chain study involving algae, Daphnia, goldfish, and guppies reared together and exposed to 1 ppm concentration of picloram over a period of 10 weeks, no effects were noted in the normal patterns of growth of the organisms (100). No adverse effects were exhibited by the guppies even after 6-month exposure to a 1 ppm concentration (100).

No data are currently available on the degradation products of picloram in fish or in lower aquatic organisms.

TABLE 16. THE LC_{50} FOR VARIOUS FISH TO PICLORAM (16)

Formulation	Fish species	Exposure time (hr)	LC_{50} (ppm)
Potassium salt	Harlequin fish	24	66
Acid	Fathead minnow	24	64
	Fathead minnow	24	135
	Rainbow trout	24	150
	Green sunfish	24	150
	Brown trout	24	230
	Rainbow trout	24	230
	Brown trout	24	240
	Brook trout	24	240
	Brook trout	24	420
	Green sunfish	24	420
	Black bullhead	24	420
	Rainbow trout	48	2.5

TABLE 17. THE 24-HR LC_{50} FOR VARIOUS FISH TO PICLORAM FORMUALTIONS (16)

Formulation	Fish species	LC_{50} (ppm)	Temperature (°F)
Acid	Bass	19.7	75
	Bluegill	26.5	63
	Goldfish	27-36	75
	Coho salmon	29.0	63?
	Rainbow trout	34	55
Triisopropanolamine salt	Rainbow trout	279.0	60
Triethylamine salt	Rainbow trout	43.4	60
	Channel catfish	70.5	80
	Goldfish	90.6	80
Potassium salt	Channel catfish	41	80
	Bluegill	69	80

4.3 WILDLIFE

Picloram has low toxicity to warm-blooded animals (1,3,20). The LD_{50} values for several mammalian species are presented below (1):

Species	LD_{50} Value (mg/kg)
Rats	8200
Mice	2000-4000
Rabbits	2000
Guinea pigs	3000
Chicks	6000
Sheep	> 1000
Cattle	> 750

Lynn (102) reported that sheep showed no ill effects from the potassium salt formulation (25 percent active ingredient) up to 4,650 mg/kg. However, the Tordon 101 formulation produced toxic effects at 2,530 mg/kg and subsequent death in three days. Cattle were more sensitive in showing toxic effects at a rate of 1,900 mg/kg Tordon.

Chronic exposure to picloram showed little or no effects on test animals (6). Feeding studies conducted for 90 days with rats resulted in no adverse effects from dietary levels as high as 1,000 ppm (103). The only effect noted at 0.3 percent picloram in the diet was an increase in liver/body weight ratios of the females (104). Only slight to moderate pathological changes were observed in the liver and kidneys on a diet containing 1 percent (1,000 ppm) picloram. No adverse effects were noted in any animals fed a 0.3 percent triisopropanolamine salt picloram diet (104).

In long term feedings, albino rats and beagle dogs were fed picloram at a rate of 15 to 150 mg/kg of body weight for 2 years (104). No observable adverse effects were noted in either species in terms of body weight, food consumption, behavior, mortality, hematological and clinical blood study results and urine analyses results. Also, no pathological differences were found in the incidence or kind of tumors found in controlled and treated animals.

Picloram also exhibits low toxicity to birds (1). Japanese quail (coturnix coturnix) and bobwhite quail (Colinus virginianas) were fed picloram at rates ranging from 100 to 1,000 ppm in their diets without reaching the LC_{50} (105). The LD_{50} was more than 2,000 ppm for young mallard ducks (anac platyrhynachos) and for young pheasants (Phasianus colchicus) (106). The LC_{50} for adult mallard ducks and pheasants exceeded 5,000 ppm (105). Japanese quail fed up to 1,000 ppm of picloram in their diet for each of three successive generations exhibited no effects on mortality, egg production, and fertility (105).

A summary of additional feeding studies on birds is presented in Table 18 (108). Toxicological studies conducted on Tordon 101 indicate that it is more toxic than picloram (101). In a subacute oral toxicity experiment, Tordon 101 fed to 11 sheep at 0.11 mg/kg resulted in no adverse effects, but at 0.55 mg/kg resulted in 2 deaths within 10 days (107).

4.4 BENEFICIAL INSECTS

Limited studies on picloram and picloram plus 2,4-D have indicated low toxicities of these compounds to bees (109.110). The LD_{50} for both picloram and Tordon (unspecified formulation) is reportedly 15 μg/bee (109). In a study by Morton, et al. (111), newly emerged honey bees (Agis mellifera L.) fed concentrations of 0, 10, 100 and 1,000 pppm by weight of picloram in 60 percent sucrose syrup showed no reduction in half-life at any concentration tested. In fact, there was an increase noted in the half-life of bees fed the 100 and 1,000 ppmw concentrations when compared to control bees. In a study by Moffett, et al. (112), Tordon 22K and Tordon 212 applied at a rate of 4 lb a.i./acre to honey bees confined in a small water carrier volume of 20 gal/acre were non-toxic.

4.5 MICROFLORA

Picloram has very low toxicity to soil microorganisms (1,3,20). Experiments conducted by Goring, et al. (113) with 45 common soil microorganisms, including bacteria and fungi, showed that picloram had little effect on total numbers at concentrations up to 1,000 ppm. The growth of one organism, Thiobacillus thiooxidans, was inhibited at 1,000 ppm but not at 100 ppm. In addition, rates of carbon dioxide evolution, nitrification and urea hydrolysis were unaffected.

Arnold, et al. (114) showed that the growth of Aspergillus niger, as mycelial dry weight, was not depressed by addition of 0.4-5.0 ppm picloram

TABLE 18. TOXICITY OF PICLORAM TO GAME BIRDS (108)

Species	Acid Equivalent (mg/kg-feed)	Observations
Japanese quail Coturnix coturnix Japonica	100	14-day exposure, reproduction study, No effect on plumage, feathering, egg production, fertility, hatchability, mortality or weight.
	1,000	14-day exposure, reproduction study. No effect on egg production, body weight or adult mortality. Egg fertility reduced 55%, egg hatchability reduced first week but not second week of treatment. Hatchability and fertility normal first week after treatment.
	100– 1,000	Dosage increased over a period of nearly one year. No increased mortality, no decrease in consumption or body weight; no impaired reproductive effect compared to controls.
Japanese quail Coturnix coturnix japonica (5-7-day-old chicks)	100; 500; 1,000	Reproductive, three-generation study. F_o generation fed 20 weeks, F_1 generation fed 12 weeks, F_2 generation fed 8 weeks. No statistically significant difference between controls and treatments as measured by food consumption, egg production, fertility and hatchability, survival and body weight gain. No adverse symptoms noted when medicated diets were withdrawn.
Bobwhite quail Colinus virginianus	23,366	LC_{50}*
Bobwhite quail Colinus virginianus (5-7 day old chicks)	10,000	LC_{50}*
Mallard ducklings Anas platyrhynchos	500– 10,000	0% mortality*
	385,200	LC_{50}*

*5-day feeding, 8-day mortality. VSDI protocol.

in nutrient solution, although picloram tended to accumulate in the mycelia. Concentrations of picloram up to 1,000 ppm did not appreciably affect the population of the fungus.

Hameed and Foy (115) studied the effects of picloram on the growth of five soil fungi: Trichoderma virdie, Fusarium oxysporum, Helminthosporium victoriae, Penicillium lanosum, and Aspergillus flaves. All five species grew, as indicated by increases in mycelium dry weight, when cultured in modified soil extract containing 1-1,000 ppm picloram. However, all of the fungi failed to produce mycelial pads in a synthetic liquid medium lacking carbon or nitrogen but supplemented with picloram, indicating that picloram alone is not a favorable sole source growth media for the fungi.

In studies on the effect of picloram on microbial activity in three Willamette Valley soils, Tu and Collen (116) found that concentrations of 1 and 10 ppm of picloram were inhibitory to populations of Penicillia but stimulated growth of Aspergilla and Trichoderma. However, the increases in population were small and not considered important to overall soil fertility.

Investigations by Arvik, et al. (117) indicated that picloram alone or in combination with 2,4-D can inhibit the growth of certain species of algae in concentrations of 50 to 250 ppm. In a study by Hardy (118), algae were unaffected by picloram at 1 ppm in water. In other studies by Elder (119), picloram exhibited low toxicity to many fresh water and marine algae species at concentrations approaching its maximum solubility in water.

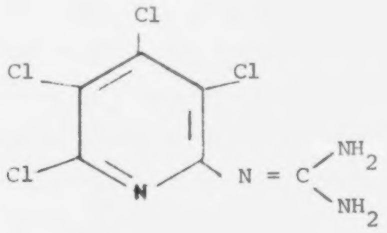
4.6 BIOACCUMULATION

Picloram is rapidly excreted by and does not bioaccumulate in mammals. In studies using carboxyl-^{14}C labelled picloram fed to dogs at levels of 100 mg/kg in the diet, 90 percent of the labelled picloram was excreted within 48 hours in the urine (103,120). Studies using rats and steers showed small residue levels in various tissues (liver, heart, fat, brain) and in blood at various feeding levels (103,121). Concentrations of 200 to 400 ppm of picloram were required in the diet of cattle to produce residues of 0.05 to 1.0 ppm in edible tissue such as fat and muscle (122). McCollester and Lang (104) found that mammals eliminate 98 percent of ingested picloram from the bloodstream and kidneys as an unchanged compound in the urine before it is able to be metabolized in the liver. Other investigations have shown that picloram is not decarboxylated *in vivo* (22).

Picloram in water is not accumulated in invertebrates or in food chains (20). *Bambusia sp.* exposed to 5 ppb of picloram in water for 567 days in a static test accumulated a concentration of 1.12 ppb. The accumulation factor (whole body, wet weight) was low at 0.25 (3). In separate experiments, the accumulation factors for catfish was 0.023 for picloram, and 0.050 for the picloram metabolite 6-hydroxy-3,5-dichloro-4-aminopicolinic acid (3). A summary of the accumulation factors in several other aquatic and terrestrial organisms is shown in Table 19.

5.5 MISCELLANEOUS

As indicated in Section 4.2, picloram and its salts exhibit low toxicity to fish. Recent studies by Sargent, et al. (94) have found that certain picloram ester formulations may be more toxic to fish than picloram and its salts, due to the presence of the toxic impurity 2-(3,4,5,6-tetrachloro-2-pyridyl)-guanidine in the ester formulations.



Other known impurities of picloram ester formulations include:

4-amino-3,5,6-trichloropicolinonitrile
4-amino-2,3,5,6-tetrachloropyridine
6-amino-3,4,5-trichloropicolinic acid.

These 3 impurities are not toxic to fish at concentrations of 10^{-4} M or less.

In view of the phytotoxicity of picloram (see Section 4.1), various thickening and sequestering agents are often added to picloram formulations and spray mixes to reduce the potential for drift (20). As indicated in Table 8, Tordon 101 and Tordon 101R contain a glycol derivative sequestrant. Data are unavailable on the exact composition and the environmental and health hazards, if any, of these sequestrants.

TABLE 19. CONCENTRATION FACTORS* OBSERVED FOR PICLORAM IN SOME AQUATIC AND TERRESTRIAL SPECIES (20)

SPECIES	MEDIUM	COMPOUND	TISSUE	CONC. FACTORS* BASED ON a.e. OF PICLORAM	TIME SCALE	REFERENCES
Daphnia	Water	K-salt	whole body	1.0	7 weeks	123
Mosquito fish	Water	Acid	whole body	0.02	18 days	124
Dairy Cattle	Diet	K-salt	Milk	0.0003	2 weeks	125
Steers†	Diet	Acid	Blood	0.001	2 weeks	126
			muscle & fat	<0.0005		
			kidney	0.01		
Sheep	Diet	Acid	Blood	0.001	1 week	126

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*/
Concentration in tissue, a.e./concentration in water or diet, a.e. A factor of one or less means no accumulation greater than that found in the medium of exposure, i.e. diet or water, over the time scale of the exposure. These numbers are not considered absolutes but only indicators since time-dose-dependent studies *per se* have not generally been carried out.

†/
Upon continuous exposure, residues reached a plateau within three days. The concentration factor, ppm-blood/ppm-diet, was independent of time for the remainder of the study and the concentrations in the blood are nearly directly proportional to the concentrations in the feed.

Picloram and its derivatives have been involved in a number of reported incidents of environmental contamination (58,92,127). One of the best documented incidents occurred in 1968 in which picloram used in agriculture resulted in contaminated ground water near Kimball, Nebraska (92,127). When the ground water was used for irrigation, major plant damage occurred in gardens, croplands, and commercial greenhouses in Kimball. Other alleged incidents have involved damage to agricultural crops, wildlife and domestic animals (92). Many of these incidents are currently under investigation by EPA and have not yet been confirmed (92).

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Common Name: Simazine

Chemical Name: 2-chloro-4,6-bis(ethylamino)-s-triazine

Major Trade Name: Princep

Major Applications in Forestry: Used primarily in the Pacific Northwest for site preparation, conifer release and nursery applications for grass and broadleaf weed control.

SUMMARY

Most of the available information on the fate of simazine in soil and water is the result of laboratory and/or field studies with agricultural systems. Very little data are available on or in connection with applications to forests.

The principal mechanism of simazine uptake by plants is through the roots. Simazine is considered a stable, persistent herbicide and may persist in phytotoxic concentrations for over a year in agricultural soils. Simazine degrades via chemical and microbial routes. High concentrations of soil organic matter, such as may be present in forest soils, as well as low temperatures and high pH, tend to increase its persistence. At pH 4, the degradation half-life in soil is 10 years; at pH 2, 40 days. Simazine losses due to volatilization from agricultural soils are very small. Such losses are expected to be even less from forest soils due to lower temperatures. Although simazine decomposes by uv light, the extent of photodecomposition in forest systems is expected to be very low.

Simazine is considered a low solubility, low mobility herbicide. Leaching and desorption of simazine are lowest in soils with high organic matter content, and hence should be low in forest soils. It is very slightly soluble in water. Its half-life in water is reportedly 50-70 days, with 99 percent loss 12 months after application.

Simazine is phytotoxic to numerous non-target plant species. It is extremely toxic to very young, recently emerged red pine seedlings. It is only slightly toxic to fish, lower aquatic organisms, and reportedly has no insecticidal activity. It is relatively nontoxic to mammals. Bioaccumulation is low in fish and microorganisms, and nil in animals.

Inert ingredients present in simazine formulations are not considered hazardous.

1.0 INTRODUCTION

Simazine is a selective herbicide and soil sterilant that has been widely used in crop and noncrop applications since its discovery, along with atrazine and other s-triazine herbicides, in the early 1950's in Switzerland (1). It is used in forestry and agricultural applications primarily for highly effective control of annual and perennial grasses and shallow-rooted broadleaf weeds; it is less effective on deep-rooted broadleaf weeds such as Canada thistle, birdweed, and St. Johnswort (2).

In the forest industry simazine is used primarily in the Pacific Northwest for site preparation, in conifer release and in nursery applications alone or in combination with atrazine (3,4). Usual application rates are 3 to 4 lb of 80 percent active ingredient in 10 gallons water/acre for site preparation and conifer release; and 1.6 to 3.8 lb of 80 percent active ingredient in 10 to 25 gallons water/acre in nursery applications (4). Princep 80W is one of the principal wettable powder formulations used. The primary method of application is the ground spot method (3), although aerial broadcast is also used (3,5). In areas west of the Cascades, applications are usually recommended for late winter or early spring (2). The most desirable time to make application is in late February or March. Applications made after April 1 may not receive enough moisture to carry the materials into the root zone of the weeds. In areas east of the Cascades, suggested applications are for early fall (2). Simazine is reportedly also used to a limited extent in the south in combination with atrazine.

Agricultural uses of simazine include application to corn, established alfalfa and bermuda grass, fruits, nuts and turf grass (6). At high rates of application, it is also used for nonselective weed control in industrial areas, in airports, and railroad rights-of-way (7). Simazine is also used for algae control in ponds, fountains, recirculating water cooling towers, and large aquariums and swimming pools (8,5). After uptake by plant roots or algae, simazine exerts its toxic action by inhibiting photosynthesis by arrestation of the "Hill" reaction in chloroplasts (9).

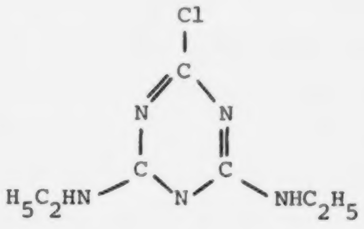
Simazine is manufactured domestically by Ciba-Geigy Corporation under the trade name Princep (6). In the U.S., simazine is also marketed under the trade name Aquazine for control of algae and aquatic weeds. Simazine is also available from foreign producers under the following trade names (5):

- Cekusan
- Framed
- Gesatop
- Primatol
- Simadex
- Simazol

Simazine is formulated as a wettable powder containing various percentages of technical grade active ingredient; the remainder of the formulation consists of various diluents such as chalk or kaolin (6,8). Simazine is also formulated with amitrole as Simazol (6).

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENTS

The chemical nomenclature for simazine is 2-chloro-4,6-bis(ethylamino)-s-triazine:



Simazine is a white crystalline solid with a melting point of 225 to 227°C. Solubility data in water and organic solvents as a function of temperature are shown below (5):

Solvent	Temperature, °C	ppmw
Water	0	2
	20	3.5
	85	84
Chloroform	20	900
Methanol	20	400
n-Pentane	25	3
Petroleum ether	20	2

Simazine exhibits very low volatility. Vapor pressure data are presented below as a function of temperature (5):

Temperature, °C	mm Hg
10	9.2×10^{-10}
20	6.1×10^{-9}
30	3.6×10^{-8}
50	9.0×10^{-7}

3.0 ENVIRONMENTAL FATE

Very little environmental fate data have been published in connection with the use of simazine in forests. Most of the fate information discussed in this section is based on data reported for non-forest applications.

3.1 UPTAKE AND METABOLISM IN PLANTS

Laboratory experiments conducted on the uptake of simazine on corn, sorghum, cereals, weeds and other plants have shown that the principal mechanism of uptake in through the plant roots and that uptake occurs rapidly in the presence of adequate moisture which carries the herbicide to the root zone. The studies also indicate that the uptake increases with increasing concentration of simazine, time of exposure, temperature and decreasing relative humidity (1). Studies using radiolabelled triazine herbicides have shown that they translocate rapidly and distribute evenly throughout the plant system into all aerial parts of the plant, with some accumulation in the marginal zones of the leaves, particularly in susceptible species (1). Simazine does not penetrate readily through plant leaves and foliar applications are generally ineffective; however, studies have shown that foliar penetration occurs and is enhanced by plant cuticle damage, by hail damage to leaves, and by surfactants on the leaves or in simazine formulations (10).

Metabolic degradation of simazine in plants occurs via 4 major mechanisma (1,8,11): (1) hydrolysis of the 2-chloro group to give hydroxy simazine; (2) N-dealkylation of the side chains; (3) conjugation with glutathione or amino acid compounds such as γ-glutamylcysteine at the 2-position of the triazine ring; and (4) s-triazine ring cleavage. Ring cleavage of intact simazine is a difficult and slow process and occurs to a minor extent over long periods of time. N-dealkylation is thought to proceed via a free radical mechanism, as indicated in studies by Plimmer, et al. (12). Ammelide and ammeline have been reported as products of further degradation following

N-dealkylation (8). In general, the route and rate of degradation vary with plant type, stage of growth and site of entry into the plant. The metabolism rates are more rapid in tolerant plants than in susceptible plants.

Extensive studies have been conducted by Montgomery and Freed (13), Castelfranco (14), and Gysin and Knusli (15) on the root uptake and metabolism of simazine in corn and maize; these studies indicate rapid uptake and decomposition for simazine. Degradation occurs in the presence of a corn enzyme (thought to be a benzoxazine derivative) (16) via hydrolysis of the 2-chloro group to produce 2-hydroxy simazine followed by ring cleavage and/or conjugate formation with the plant acids (see Figure 1) (8). The metabolism of simazine in corn is apparently very rapid and is completed before simazine is translocated to the leaves.

Hydrolysis and conjugation of simazine result in a complete loss of phytotoxic properties. Plant species which hydrolyze and/or conjugate simazine are most resistant to the herbicide. N-dealkylation of simazine results in only partial loss of phytotoxicity, and species using this route of degradation have moderate resistance to simazine (1).

3.2 FATE IN SOIL

The fate of simazine in soil can be described in terms of volatilization, photodecomposition, leaching, adsorption, runoff, and chemical and microbial degradation. These factors are discussed in the sections below.

3.2.1 Volatilization

The extent of simazine volatilization from soil is not fully known. Simazine is known to dissipate from treated areas by volatilization, but it is generally held that this does not take place to a significant extent (5), presumably due to the extremely low vapor pressure of simazine. Laboratory studies by Foy (17) of simazine on planchets at 25° and 60°C showed very little loss of simazine, even at the higher temperature. In another laboratory study measuring triazine losses from 5 soils as a function of soil type (18), simazine was observed to volatilize only very slightly and less than atrazine. This is reasonable due to the fact that simazine has a lower vapor pressure than atrazine.

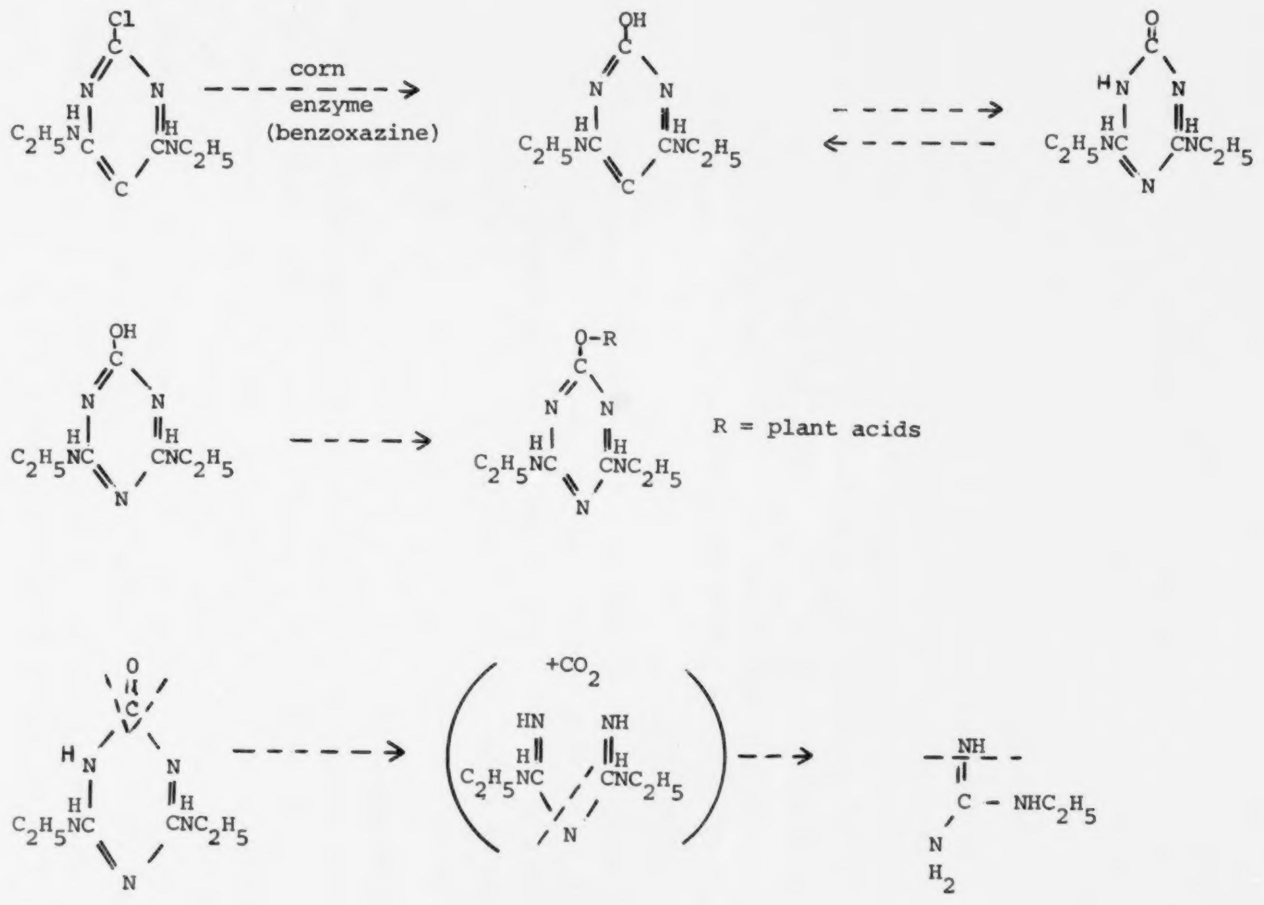

corn
enzyme
(benzoxazine)
R = plant acids
+CO2

Figure 1. Metabolism of Simazine in Corn (8)

In the forest the extent of simazine volatilization from soil due to sunlight exposure may be less than that in an agricultural field due to increased shading. In addition to temperature, volatilization if also affected by soil moisture, with increased volatilization from drier soils (18,19). Also because simazine is somewhat amphoteric in nature, the pH of aqueous solutions may be expected to influence its volatility; the extent of this influence has not been determined (10).

3.2.2 Photodecomposition

Simazine can undergo photodecomposition under uv radiation (20). The rate of photodecomposition and factors influencing it are not fully understood (5). It is, however, generally held that under normal climatic conditions, loss of simazine from soil and foliage surfaces by photodecomposition is insignificant (5). It is possible that photodecomposition occurs to some extent in agricultural fields where high temperatures and prolonged sunlight may prevail (5), but these conditions are not considered typical of the forest environment.

The photodecomposition of simazine on metallic and non-metallic surfaces has been studied to a limited extent in the laboratory (21). In a study by Jordan in 1965 (22), simazine on aluminum planchets decomposed upon exposure to sunlight and uv light. Different degradation products were reportedly obtained for each light source.

3.2.3 Adsorption and Leaching

Simazine is considered to be a low solubility, low mobility herbicide (16). It is readily and strongly adsorbed on soil particles (5,8). The extent of adsorption is primarily a function of soil type and is also affected by soil temperature, moisture and pH (23,24). As indicated in studies by Goring (25) and other researchers (5), soil organic matter is the principal soil parameter responsible for adsorption, with increasing organic matter resulting in increased adsorption. Simazine is also more readily adsorbed on clay soils than on soils with low clay content (5).

The amino groups of the simazine impart weakly basic properties to the molecule; at higher pH levels simazine may lose its affinity for negatively charged clay soil particles and desorb more readily from clay soils (8,26).

Consequently, acidic conditions would be expected to promote adsorption on clay soils. In a study by Sheets (26), simazine was removed from solution by a cationic exchange resin and not by an anionic exchange resin, thus indicating that under the conditions tested, simazine exhibited acidic properties and was electrically positive.

The adsorption capacity of a given soil for simazine affects its potential for leaching of simazine. The leaching tendency is lower in those soil types and under those conditions which promote adsorption. Leaching is known to be more pronounced in sand and clay-type soils than in soils with high organic matter content (27). This was confirmed in a laboratory study on 3 Florida soils (i.e., Lakeland fine sand, Greenville fine sand, and Everglade muck) in which the least penetration (to a one-inch depth) was achieved with the high organic muck soil (27). In this study simazine was also shown to leach at much lower rates than atrazine. In a separate study simazine was shown to migrate to a depth of 6 inches with application of one inch of water (28). Other tests have indicated that for several months after application, the greatest amount of simazine remains in the upper 2 inches of soil (5). Smith, et al. (29) observed that simazine applied to Canadian irrigation ditches at a rate of 22.4 kg/ha remained primarily in the top 7.5 cm of soil after 3 growing seasons, whereas atrazine became distributed uniformly throughout a 90-cm soil depth. Marriage, et al. (30) found that residues of simazine applied for 9 consecutive years at a rate of 4.5 kg/ha to the same plots of a peach orchard located on a sandy loam soil near Harrow, Ontario, were confined to the upper 15 cm of the soil profile and that the majority of the herbicide remained in the 0-5 cm soil layer. The maximum residue level found was 1.6 kg/ha of simazine in the top 15 cm of the soil profile.

An empirical worst-case model was proposed by Hartley (31) describing the pattern of leaching of simazine at 2 application rates using soil having no adsorptive capacity and 20 percent pore volume. At 1 lb/acre, it was postulated that one inch of rain could dissolve all of the simazine and produce a saturation zone in the upper 5 inches of soil. According to the model, further rain would move the zone downward as a 5-inch band. At 10 lb/acre, 10 inches of rain would dissolve the simazine and give a 50-inch band. Soil with increased adsorptive capacity would reduce the leaching tendency. Even though leaching of simazine from forest soil has not been studied, the extent of such leaching is expected to be lower than that in agricultural soil because of the higher organic content of the forest soil.

Limited data are available on rates of simazine runoff resulting from rainfall after forest or crop applications. In a study performed by the U.S. Department of Agriculture to determine the pathways and quantities of simazine and other herbicides transported from Appalachian watersheds (32), the highest concentration of simazine (1.2 ppm) was present soon after application in runoff on 0.4 to 3.5 ha agricultural watersheds and declined rapidly in later rainfall events. A maximum of 6 percent and an average of 2 percent of the applied simazine were transported in the runoff. Less runoff occurred from no-tillage rather than from conventionally tilled fields.

Several studies have been conducted on atrazine runoff which indicate that although atrazine is only very slightly soluble in water, a potential exists for buildup in local streams/rivers due to runoff after heavy rainfall (33). Because of the lower solubility of simazine compared to atrazine (5 ppm vs. 70 ppm at 25°C), runoff via solubilization would be expected to be somewhat less for simazine than for atrazine.

3.2.5 Chemical and Microbial Degradation

In soil simazine is considered to be a stable, persistent compound (29). According to Sheets (34), simazine residues may persist in agricultural soils at phytotoxic levels to sensitive plants for over one year. Its persistence also makes it valuable for long term weed control (9). The half-life in soil is estimated at 4-6 months; 90 percent loss was observed after 10 months at 85°C (28). In a laboratory study using a terrestrial microcosm chamber simulating a forest ecosystem and containing synthetic soils and vegetation (Douglas fir and alder seedlings, etc.), total soil residues of simazine were 0.18 ppm after 26 days following application of 0.25 lb/acre simazine (35).

The persistence of simazine is a function of soil type, with less persistence in soils with high organic matter content (36,37). Aelbus and Homburg in 1959 (38) showed simazine to be less persistent in clay and peat soils than in sandy soil 3, 6, and 11 months after application. Simazine residues have been monitored in high organic content Woodbridge loam soil in a young Fraser fir (Abies fraseri pursch pois) plantation plot in Wolcott, CT, to which 4, 8, 12, and 16 lb/acre of simazine were applied (39). The results, shown in Table 1, indicate that even in the fall after spring application, simazine residues were generally less than 1 ppm.

In a study by Walker (40) using sandy loam soil, the time required for disappearance of 50 percent applied simazine varied from 37 days at 25°C (13 percent soil moisture) to 243 days at 15°C (7 percent soil moisture). Simazine persists slightly longer than atrazine in most soils, but in some soils the two are about equally persistent (41).

In addition to soil type, the persistence of simazine is also a function of pH, temperature and moisture. In a study of persistence of simazine in corn and soybean production fields, Slack, et al. (42) determined that the persistence increased with increasing pH. A number of other laboratory and field studies by Burnside, et al. (43), Harris and Sheets (44), and Harris, et al. (45) have shown that simazine is more persistent in colder drier climates than warmer, wetter ones. A mathematical model was developed by Walker (46) to describe and predict the effects of soil temperature and moisture on degradation rates for four herbicides including simazine. In the model, temperature effects are characterized by the Arrhenius equation: $\ln k = -E_a/RT$ where k is the rate constant of degradation and E_a is the experimental activation energy, and moisture effects are characterized by the empirical equation of the form: $H = AM^{-b}$ where H is the half-life at moisture content M, and A and b are constants derived from laboratory measurements; the constant b gives a measure of the moisture dependence of degradation. The predicted relative order of persistence of the 4 herbicides was verified in field experiments on sandy loam soils under various conditions of temperature and moisture. To date, the model has not been tested against other soil types.

The persistence of simazine in bottom sediments in ponds has also been studied in connection with its use for algae control. Mauck, et al. (47) reported simazine residues of 0.07 and 0.32 μg/ml in mud residues from 4 ponds after 346 days and application of 1.0 and 3.0 μg/ml, respectively (47). The concentration of simazine plateaued approximately 35 days after application at levels of roughly 0.1 μg/ml and 0.5 μg/ml, respectively.

TABLE 1. SIMAZINE RESIDUES (PPM) IN SOIL IN FRASER FIR PLANTATION (39)

Rate #/acre	0				4				8				12				16			
Year	68	69	70	71	68	69	70	71	68	69	70	71	68	69	70	71	68	69	70	71
Depth																				
0-3"	0.12	--	--	0.00	0.54	0.28	0.00	0.00	1.23	0.15	0.07	0.07	1.12	0.31	0.00	0.09	1.45	0.95	0.10	0.00
3-6"	0.09	--	--	0.00	0.14	0.17	0.00	0.00	0.30	0.12	0.00	0.05	0.32	0.19	0.00	0.06	0.29	0.17	0.00	0.00
6-12"	0.22	--	--	0.00	0.12	0.36	0.00	0.00	0.09	0.18	0.11	0.07	0.19	0.22	0.00	0.00	0.31	0.18	0.00	0.05

Simazine degradation in soil occurs via both chemical and/or microbial routes. A brief review of the factors affecting each of these degradation pathways follows.

Chemical Degradation--

Hydrolysis is the major chemical degradation reaction of simazine in soil. The reaction is first order and involves hydroxylation of the carbon-chlorine bond to give hydroxy simazine (1,48). The rate of reaction is pH dependent, with increasing hydrolysis at lower pH. At pH 4, the half-life of the acid-catalyzed hydrolysis of simazine is 10 years, at pH 2, 40 days (15).

As with atrazine, hydrolysis may be catalyzed by certain soil compounds. Nucleophilic compounds in soil including Fe/Al ions promote nucleophilic displacement of -Cl with -OH at high pH, whereas humic acid and various soil colloidal particles catalyze hydrolysis at low pH. The low pH hydrolysis results from the protonation of ring or chain nitrogen atoms and subsequent cleavage of the C-Cl bond (49).

Increasing temperature and moisture also favor hydrolysis of simazine (50,51,52).

In addition to hydrolysis, N-dealkylation of simazine is a possible degradation route in soil; no information has been reported on the rate of this reaction and factors influencing it. Also not reported are data on subsequent degradation of hydroxy and dealkylated simazines.

Microbial Degradation--

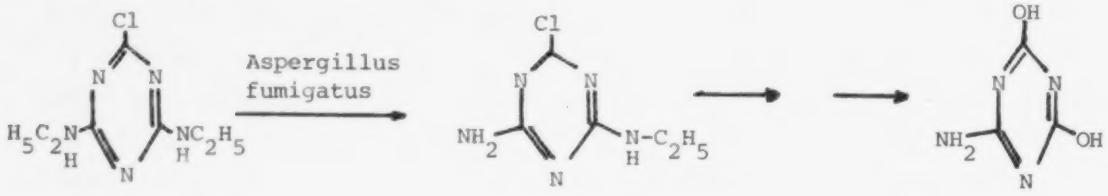
Simazine in soil is subject to microbial degradation. A list of microorganisms capable of degrading simazine is presented in Table 2. Factors influencing microbial growth in soil include soil moisture, temperature, pH, soil type and presence of nutrients (1), but very few studies have been performed measuring the effect of these factors on microbial degradation of simazine. Three major routes for biological degradation are: N-dealkylation, hydrolysis, and ring cleavage.

N-dealkylation is one of the primary mechanisms of microbial degradation and has been studied by a number of investigators in recent years. Studies by Kearney, et al. (53) have shown that simazine dealkylation by *Aspergillus*

TABLE 2. LIST OF MICROORGANISMS WHICH DEGRADE SIMAZINE IN SOIL

Name of Microorganism	Reference
1. Actinomycetes	
Streptomyces sp.	56
2. Fungi	
Penicillium purpurogenum	56
P.cyclopium	57
P.lano-coeruleum	57
Aspergillus ustus	56
Fusarium oxysporum	57
F.avenaceum	57
Cylindrocarpon radicicola	57
Stachybotrys sp.	57
Xanthochrous pini	58
Coriolus versicolor	58
Penicillium citrinum	58
Penicillium notatum	58
3. Bacteria	
Corynebacterium sp.	8
Escherichia coli	8
Bacillus mesentericies	59,60
Bacillus mycoides	59,60
Bacillus cereus	59,60
Bacillus agglomeratus	59,60
Bacillus idosus	59
Pseudomonas fluorescens	59

fumigatus Fres. results in the formation of 2-chloro-4-amino-6-ethylamino-s-triazine. Recent studies by Plimmer (12,54) have demonstrated that a free radical mechanism may be involved in the reaction. Subsequent metabolism of the 2-chloro-4-amino-6-ethylamino-s-triazine results in further dealkylation or deamination, followed by dehalogenation of the 2-chloro group to give ammelide. The following degradation pathway has been determined (11,55):



Simazine

2-chloro 4-amino-
6-ethylamino-s-triazine

Ammelide

Limited information is available on hydroxylation and ring cleavage of simazine by soil microorganisms (50,61,62). Hydroxylation is regarded as an initial reaction in microbial degradation of simazine and other triazines (63). Ring cleavage is a minor degradation reaction in soil. In a study by Ragab and McCollum (64), only a few percent of labelled CO_2 was produced from simazine uniformly labelled with ^{14}C in the triazine ring. In a separate study by Süss (65), it was noted that microbial degradation reactions of simazine are lengthy and occur in successive phases. Approximately 2.5 percent of ^{14}C- ring label of simazine was evolved as $^{14}CO_2$ from different soils within five weeks. This period was followed by a lag phase of up to 15 weeks, after which a second period of $^{14}CO_2$ evolution started and continued up to 30 weeks. Depending on the soil type, the cumulative amount of $^{14}CO_2$ liberated varied from 6 to 17 percent. In a subsequent study by Süss (66), when simazine adsorbed to peat was incorporated into various soils, a substantial increase in the liberation of $^{14}CO_2$ was observed in contrast to the control in which simazine was added directly.

Both dealkylated and hydroxylated simazine degradation products are subject to further microbial degradation (1). Recent studies have shown that degradation of both types of products may give rise to common metabolites, such as 2-hydroxy-4-amino-6-alkylamino-s-triazine (1,67).

3.3 PERSISTENCE IN WATER

Simazine is considered to be "moderately" persistent in water. The half-life in water is reportedly 50-70 days, with 99 percent loss 12 months after application (28). When applied to ponds for weed and algae control, the average half-life of simazine is 30 days (5). The hydrolysis of simazine in aqueous solution has been studied as a function of temperature and pH over a period of 28 days (8). Based on the results, hydrolysis rate constants and half-lives were calculated for temperatures of 30, 50, 70°C and pH levels ranging from 0.1 to 13. The calculated data indicated no significant hydrolysis of a simazine over the test period in the pH range 5-9 at any of the test temperatures. Slow hydrolysis (half-life of about 4 months) occurred at an elevated temperature of 70°C at pH 7, and the rate of hydrolysis generally increased with both increasing or decreasing pH from pH 7.0.

The persistence in ponds is dependent upon many factors including the level of algae and weed infestation, and pond temperature (5). Mauck, et al. (47) studied the decay of simazine applied to four 0.25 acre ponds. The results, summarized in Table 3, indicate that simazine residues in water were directly proportional to rates of application, and seldom exceeded one-third to one-half of the total amount applied. Simazine was still present in the water 346 days after the first application, and 456 days after the second application. In a study conducted by Ciba Geigy (8) in 1973, 0.25 ppm active ingredient simazine was added to the littoral zone of Findley Lake, N.Y. After 5 days and 15 days, simazine levels in epiliminon (0-15 feet) water was at about the same level as initially (0.25 ppm); hypoliminon (15-35 feet) water contained about 0.03-0.04 ppm on both days. Results of a number of other studies on the persistence of simazine in ponds indicate that the time for residues to decrease by 90 percent varied widely from 15 to 247 days (8).

The rate of simazine photodecomposition in water is extremely slow, as measured under laboratory conditions, and is not expected to be significant in the environment. Laboratory photolysis of simazine under uv radiation (2200°A) in water and other hydrolytic solvents (e.g., methanol) was shown to result in the formation of 4,6-bis(ethylamino)-s-triazine (12).

TABLE 3. SIMAZINE RESIDUES IN FOUR PONDS AT FISH PESTICIDE RESEARCH LABORATORY, COLUMBIA, MISSOURI (47)

Time after treatment (days)		Treatment concentration (µg/ml)		
	0.1	0.3	1.0	3.0
-2	ND	ND	ND	ND
March 29, 1970----Simazine applied----				
1	0.02	0.10	0.45	0.87
3	0.05	0.23	0.42	0.58
8	0.07	0.18	0.37	0.65
29	0.05	0.17	0.48	0.86
45	0.02	0.04	0.22	0.66
50	0.02	0.12	0.29	0.52
72	0.02	0.05	0.25	0.59
91	0.02	0.05	0.32	0.62
114	0.02	0.11	0.30	0.50
134	0.01	0.04	0.32	1.0
155	0.01	0.05	0.22	0.74
176	0.01	0.08	0.30	1.2
197	0.01	0.04	0.19	0.45
220	<0.01	0.02	0.21	0.52
246	<0.01	0.02	0.11	0.16
346	<0.01	0.03	0.09	0.14
April 2, 1971----Simazine applied----				
5	0.11	0.66	0.90	1.2
18	0.12	0.28	1.4	2.1
28	0.11	0.36	1.4	2.5
40	0.13	0.34	1.5	2.2
54	0.15	0.35	1.5	3.3
81	0.08	0.20	0.94	1.2
99	0.07	0.25	1.0	2.0
110	0.07	0.21	1.0	2.6
123	0.03	0.13	0.65	1.7
138	0.06	0.20	0.82	2.2
165	0.07	0.22	0.90	2.4
193	0.06	0.20	1.2	2.5
456	0.01	0.07	0.42	0.50

*ND = none detected

4.0 IMPACTS OF NON-TARGET PLANTS AND ORGANISMS

4.1 PLANTS

Simazine has been shown to be phytotoxic to non-target forest species under certain application conditions. In a study by Kozlowski and Kuntz (68), simazine (0.5 and 1 lb active ingredient/acre) sprayed directly on the foliage of young recently-emerged red pine seedlings resulted in severe injury including extensive browning and curling and death. No harmful effects were reported on older seedlings. Simazine applied as a pre-emergence spray also caused severe damage in terms of seedling growth (68).

Simazine has been shown to have significant effects on the form, growth and color characteristics of balsam fir Christmas trees (68). Firs treated with 12 lb a.i./acre simazine or fertilizer-simazine combination displayed higher crude protein and ash content and were darker green in color and more succulent than controls. The treated trees were consequently much more attractive to browsing deer than control trees. Results further indicated that simazine has the potential to improve the quality of non-commercial shrubs and trees in peripheral areas to buffer the impacts of deer on commercial operations.

Simazine exhibits phytotoxicity to a number of non-target agricultural and orchard crops, including a wide number of monocotyledonous and dicotyledonous plants (9). Simazine has caused injury to oats following use on a previous corn crop (9). Crop injuries following application of simazine in preceding growing seasons have also been encountered in eastern Europe (69). In a study by Fischer and Lange (70) on phytotoxic responses of fruit trees to simazine and other herbicides, 20-year old bearing Elberta peach trees growing in sandy soil were severely injured at simazine application rates of 3, 4, 8, and 16 lb a.i./acre in the late spring followed by flood irrigation 20 acre-inches of water in two months. At and above 4 lb/acre simazine was excessively toxic causing severe chlorosis and burns on the foliage over most of the trees; 3 lb/acre caused considerable chlorosis. No simazine residue was found in the peach fruit up to the highest rates, i.e., 16 lb/acre. Less phytotoxicity was observed in soils with 2.1 percent organic matter content as opposed to the sandy orchard soil; even above 4 lb/acre, only slight symptoms were observed. Applications of 3.2, 6.4, 12.8 and 25.6 lb/acre of simazine repeated annually to plots of Emperor variety grapes located in Davis, California, gave no evidence of adverse effects in studies conducted by Leonard (71).

Studies by Singh, et al. (72) have shown that protein levels in various crops is increased when sublethal concentrationf of s-triazine compounds are applied. Foliar applications of 2 or 5 mg/l of simazine (generally applied until runoff occurred) increased the protein content of seeds of peas and sweet corn growing under field conditions. A similar application of 0.5 or 1.0 mg/l of simazine increased the protein content in pods of bush beans and leaves of spinach under field and/or growth room conditions. Results of quantitative analyses indicated that the soluble amino acid content was higher in the treated bush bean seeds and spinach leaves. In addition, the Fe content in the bush bean seeds and the Fe, Mg, P, and K contents in spinach leaves were higher in the treated plants than in the controls.

4.2 FISH AND OTHER AQUATIC ORGANISMS

Simazine is considered to be only "slightly" toxic to fish and lower aquatic organisms. Toxicological investigations conducted on rainbow trout and bluegill sunfish have shown simazine to have very low toxicity toward these species (5) (see also Table 4). Results of toxicological investigations conducted by Mauck, et al. (47) on the distribution of 0.1, 0.3, 1.0, and 3.0 µg/ml simazine in four 0.25-acre ponds are summarized in Table 5. The results indicate that simazine may persist in fish for more than one year. As noted in the table, residue concentrations are highest immediately after simazine application, but subsequently decline.

The effects of continuous exposures to simazine on: (1) daphnid reproduction, (2) midge emergence, and (3) growth, reproduction and survival of fathead minnows were conducted by Mayer and Sanders (73) using flow-through diluter systems. A second study was also undertaken with fathead minnows using a simulated use-pattern exposure. No adverse effects were observed on daphnid reproduction with simazine concentrations of 0.25 to 3.0 mg/l, but midge emergence was temporarily delayed in the 0.66 and 2.2 mg/l simazine range. Fathead minnow egg hatch and fry growth were reduced in continuous simazine exposures to a simazine concentration of 1.7 mg/l, and no adverse effects were found with simazine in the use-pattern exposure.

TABLE 4. FISH TOXICITY OF SIMAZINE (8)

Species	Toxic Effect
Mirror Carp	First toxic signs were noticed after 8 hours at 1g/L
Rainbow Troup	Toxic signs after about 4-8 hours at a concentration of 0.1g/L
Bluegill	Concentrations in small test ponds of up to 5 ppm caused no noticeable effect when held in this concentration for a period of 7 weeks. Terbutryn, the positive control, killed small bluegill at a concentration of 5.0 ppm.
Bluegill and Channel Catfish	LC_{50} values for Princep 80W were greater than 1000 ppm for both species at all intervals up to 96 hours after initial exposure.
Fathead Minnows	No effect level of simazine after 96 hours exposure was 2.5 ppm.
Oysters	Simazine at 1.0 ppm does not inhibit shell growth nor cause any mortality. DDT caused 50% reduced shell growth at 0.24 ppm and 35% mortality at 0.5 ppm.
Pink Shrimp and Mud Crab	The no-effect level for Pink Shrimp was 75 mg/L and 1000 mg/L for Mud Crab after 96 hours of contact with simazine.

Very little data are available on the degradation products of simazine in fish or lower aquatic organisms. In one study on the metabolism of simazine in fish (8), the major portion of the extractable residues in fish tissues consisted of the parent herbicide plus the mono- and di-deethylated derivatives. Small amounts of the hydroxy simazine and its metabolites were also found.

4.3 WILDLIFE

Simazine is considered of "low" toxicity to warm-blooded animals. The acute oral LD_{50} for rats, mice and rabbits is greater than 5000-10,000 mg/kg (5,8). Two-year chronic oral feeding studies in which male and female rats were given daily dosages of simazine at various rates as high as 100 ppm in

TABLE 5. CONCENTRATIONS OF SIMAZINE RESIDUES IN FISH (LEPOMIS MACROCHIRUS) FROM FOUR PONDS AT FISH PESTICIDE LABORATORY, COLUMBIA, MISSOURI (47)

Time after treatment (days)	Treatment concentrations (μg/ml) 0.1	0.3	1.0	3.0
-2	ND*	ND	ND	ND
March 29, 1970 - simazine applied				
1	0.86	0.49	0.95	2.0
3	0.05	0.29	0.17	0.5
8	0.08	0.11	0.69	0.8
15	0.04	0.09	0.27	0.6
29	0.05	0.11	0.20	0.6
86		0.03	0.06	0.8
114			0.18	0.4
142		0.03	0.55	0.7
176		0.01	0.01	0.1
197		<0.001	0.04	0.1
367	0.01	0.3	0.35	0.3
April 2, 1971 - simazine applied				
31		0.33	1.4	1.6
110	ND	ND	0.42	0.6
143	ND	ND	0.004	0.0
456	ND	ND	0.006	0.0

*ND = none detected

the diet resulted in no observable systemic toxicity due to ingestion (47). Little data are available in the literature on toxicities of simazine to wildlife. A toxicological investigation on bobwhite quail and mallard ducks has reportedly shown simazine to have very low toxicity (5,28); no mortality was observed at treatment levels as high as 5000 ppm.

Dietary levels of 2.0 and 20.0 ppm simazine given to mallard ducks before and during normal egg production cycles had no observable ill effects on reproductive capacities (74).

4.4 BENEFICIAL INSECTS

Limited studies conducted on simazine have shown no insecticidal activity at usual application rates (5,28). According to Beran (75), simazine is "harmless" to bees. In a study by Sonnet (76), addition of simazine to carbaryl and other insecticides at sublethal insecticide doses fed to bees showed no increase in mortality.

In an experimental program on the effect of simazine on worms (nematodes, enchytraea and annelides) and soil mites (acari) in an experimentally planted forest garden and a grass-covered pine culture near Munich, Germany, Baimber, et al. (77) found that high dosages of simazine (5 and 7.5 kg/ha) inhibited the growth of the soil animals in the forest garden but increased the population in the pine culture. Other laboratory studies by Baimber (77) of simazine on moss mites also showed that high dosages can reduce the survival times of fasted mites.

Results of toxicological investigations conducted by Mauck, et al. (47) on the distribution of 0.1, 0.3, 1.0, and 3.0 μg/ml simazine in various insects in four 0.25-acre ponds are summarized in Table 6. The insects sampled were dragonfly nymphs and midge larvae in the control pond and the ponds treated with 0.1 and 0.3 μg/ml, and mayflies (Hexagenia sp.) in the ponds treated with 1.0 and 3.0 μg/ml. Simazine residues in these organisms were directly proportional to the amounts applied, and residues persisted for more than one year. As noted in the table, residue concentrations are highest immediately after simazine application but subsequently decline.

TABLE 6. CONCENTRATIONS OF SIMAZINE RESIDUES IN BENTHIC INVERTEBRATES (47)[*]

Time after treatment (days)	Treatment concentration (μg/ml)			
	0.1	0.3	1.0	3.0
-2	ND[†]	ND	ND	ND
March 29, 1970 - simazine applied				
3	ND	1.2	2.7	27
8	ND	ND	1.8	60
15	ND			14
29	0.20	0.50	1.7	13
86	0.03	0.20	0.70	21
114	0.03	0.08		0.80
142		0.09	0.90	2.4
176		0.10	0.20	0.90
197		0.06	0.20	1.3
367		0.04	0.10	
April 2, 1971 - simazine applied				
40	ND	ND	2.0	10
55	ND	ND	0.70	5.0
83	ND	0.50	2.1	2.5
110	0.07	0.07	0.90	6.5
123	ND	ND	0.20	2.2
138	ND	0.09	0.40	2.0
193	ND	ND	0.90	1.5
456	<0.01	<0.01	0.02	0.05

[*] Tests conducted in four ponds at Fish Pesticide Laboratory, Columbia, Missouri

[†] ND = none detected

4.5 MICROFLORA

Simazine is relatively harmless to soil microorganisms and at normal application rates, it generally has no appreciable adverse effects on total numbers in soil (78,79,80). The effects of simazine on microorganisms active in the nitrogen cycle and on cellulolytic organisms were studied in the laboratory and in the field by Torstensson (81). Although the former organisms were insensitive to simazine at normal and higher than normal field application rates, the latter organisms were stimulated by simazine at both concentrations.

Limited studies have shown minor fungicidal activity of simazine (5). However, in a study by Nayyar, concentrations of 2.5, 5.0, and 10 ppm simazine in sandy loam soil slightly stimulated the fungal populations (82).

4.6 BIOACCUMULATION

The bioaccumulation of simazine in fish and other aquatic invertebrates may be considered "low". Little or no evidence of bioaccumulation was reported in fish, dragonfly nymphs, midge larvae and mayflies in a study on the distribution of 0.1, 0.3, 1.0, and 3.0 μg/ml simazine in four 0.25-acre ponds by Mauck, et al. (47). Fish studies using static water indicated simazine residues in the range of one to two times the concentration in the water (8). Field studies in treated ponds indicated one to four times the concentration in water; the higher value was possibly due to the ingestion of aquatic plant material containing simazine absorbed from the water (8). Green sunfish exposed to 1.0 ppm simazine for three weeks under simulated pond conditions showed little bioaccumulation; all of the simazine was eliminated by the fish within 7 days when they were placed in fresh water after exposure to the simazine (83).

The bioaccumulation of ^{14}C-labelled simazine by microorganisms (daphnids and algae) in static and flowing aquatic model ecosystems was studied by Isensee and Yockim (84); the results and calculated bioaccumulation ratios, shown in Table 7, indicate that the organisms in the static studies generally reached an equilibrium tissue concentration by day one and subsequently did not accumulate appreciable additional amounts of simazine. In general, the bioaccumulation ratios are low and indicate little bioaccumulation by microorganisms.

TABLE 7. ACCUMULATION OF ^{14}C-SIMAZINE BY DAPHNIDS AND ALGAE IN AQUATIC MODEL ECOSYSTEMS (84)

Organism	Experiment	Treatment*	Days after start of experiment						
			1	3	7	15	30	35†	42
Daphnids‡	Static	0.1	0§	0 (0)#	0.1 (7)	0.01	0		
		1.0	0.01	0.01 (1)	0.03 (2)	0.02	0.02		
		10.0	0.21	0.20 (1)	0.21 (1)	0.22	0.31		
	Flowing	0.1	0.19	0.19 (32)	0 (0)	0.13	0.41		
		1.0	0.35	0.09 (53)	0.14 (19)	0.17	1.09		
		10.0	0.23	0.19 (4)	0.17 (3)	0.81	3.11		
Algae**	Static	0.1	0	0 (6)	0.01 (4)	0.01	0.01+0.01	0	0
		1.0	0.02±0.07	0.04±0.02 (4)	0.03±0.01 (2)	0.06±0.02	0.11±0.01	0.05±0.02	0.05±0.02
		10.0	0.19±0.09	0.35±0.05 (3)	0.46±0.08 (3)	0.38±0.06	0.91±0.12	0.40±0.04	0.75±0.39
	Flowing	0.1	0	0 (3)	0.20+0.19	0.09+0.08	0.04+0.07	0.04+0.04	0
		1.0	0.10	0.20±0.03 (9)	0.18±0.25 (25)	0.22±0.06	0.28±0.06	0.06±0.06	0.07
		10.0	0.06	0.23±0.03 (4)	1.15±0.39 (20)	1.72±0.64	1.54±0.44	1.27±0.31	0.92±0.46

*Concentration of simazine adsorbed to 400 grams soil (static, ppm) and theoretical concentration introduced into its water (flowing, ppb).

†After day 30 the organisms were allowed to desorb in untreated water.

‡Daphnia megna.

§Tissue concentration (ppm) based on total ^{14}C analysis (simazine plus metabolites).

#Bioaccumulation ratios (in parenthesis) = tissue concentration/water concentration.

**Oedogonium cardiacum.

Based on analysis of urine and feces samples which indicate absence of intact simazine, it is concluded that simazine is metabolized rapidly by animals and is non-bioaccumulable (2). Feeding goats and cows with 1 mg/kg simazine resulted in transient milk residues which reached a maximum concentration between 8 and 24 hours after feeding, then declined rapidly to the limit of detection within 2 to 4 days (1). Cow feeding studies at levels up to 80 ppm simazine in the total diet resulted in only trace net residues in milk (0.01 to 0.02 ppm) (8). The metabolic degradation products of simazine in animals include hydroxy simazine, N-dealkylation products (e.g., 2-hydroxy-4-amino-6-ethylamino-s-triazine), side-chain modified simazine (i.e., via oxidation of the ethyl group to carboxylic acid), and conjugation products (1,8). Hydroxy simazine, and N-dealkylation and conjugation products are generally rapidly excreted in the urine with no bioaccumulation (1).

5.0 MISCELLANEOUS

As indicated in Section 1.0, commercial wettable powder formulations of simazine contain up to 80 percent active ingredient and 20 percent "inerts". None of the inert materials are considered very toxic or hazardous.

In a study on the effectiveness of the herbicide glyphosate on various plant species, it was determined that there is an appreciable loss of activity of glyphosate if wettable powder formulations are mixed and applied with simazine (85).

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Common Name: Triclopyr

Chemical Name: 3,5,6-trichloro-2-pyridinyloxyacetic acid

Major Trade Names: Garlon 3A; Garlon 4

Major Applications in Forestry: Used on an experimental basis in the Northeast, the Pacific Northwest and the South, primarily in site preparation and occasionally in conifer release for woody plant and broadleaf weed control.

SUMMARY

Triclopyr is a relatively new herbicide which has been commercially available only in the past few years. Accordingly, very little data are available in connection with its efficacy and environmental fate and impacts. The limited available data are largely from laboratory and/or field studies conducted by the manufacturer on non-forest systems.

The mechanism of triclopyr uptake by plants is through both leaves and roots. It induces characteristic auxin-type responses in plants. Triclopyr is not considered a persistent compound in soils; it degrades rapidly, with an average half-life of 46 days. The major route of degradation in soil is via microbial decomposition. Degradation of triclopyr does not occur to any appreciable extent via chemical hydrolysis or other chemical routes in soil. Triclopyr losses due to volatilization are not appreciable.

Triclopyr is considered a mobile herbicide. Leaching and desorption are lowest in soils with high organic matter content. Because of its mobility and rapid desorption from soil particles, some loss of triclopyr due to solubilization and/or runoff may be expected following field application. Although it is stable to hydrolysis in aqueous solution, triclopyr photodegrades rapidly with a half-life of 10 hours at 25°C.

Triclopyr can cause injury to conifers, particularly at high rates of application and is not generally recommended for conifer release. When applied directly, it exhibits phytotoxicity to agricultural crops. Triclopyr has low toxicity to fish and lower aquatic organisms and does not bioaccumulate in these species. It exhibits low toxicity to wildlife and is considered non-toxic to soil microorganisms.

1.0 INTRODUCTION

Triclopyr is an auxin-type herbicide for the control of many woody plants and annual and perennial broadleaf weeds. It has only recently been registered for use in forestry and it is used primarily on experimental rather than commercial scales for site preparation (1,2,3) and occasionally in conifer release (4,5). These uses are in the Northeast, the Pacific Northwest, and the South (5,6). It is not registered for use in California (3). No quantitative data are available on the extent of the uses in the Northeast and South, although it is estimated that about 100 acres in Washington, Oregon and California were treated with triclopyr in 1979 (about only 5 of the 100 acres were in California) (3). Due to production capacity limitation, the use of triclopyr in certain regions has been restricted by the manufacturer (Dow Chemical Co.) to extend the supply and make it available to new potential users (3). Most current experimental uses in the Pacific Northwest are ground applications for stump treatment and tree injection (4,7). Recommended rates for aerial spraying are 2-3 gallons/acre (Garlon 3A) for broadcast application by low-volume ground or helicopter equipment, and one-half to one gallon/100 gallons water for high volume, full spray coverage (4,8). Triclopyr may be used in combination with 2,4-D, Tordon 101, Esteron 99, or DMA 4 for forest site preparation (1,9,10).

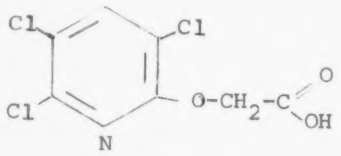
According to the manufacturer, triclopyr is effective for the control of the following woody species: alder, arrowwood, ash, aspen, beach, birch, blackberry, blackgum, cascara, chamise, choke cherry, cottonwood, crataegus (hawthorn), dogwood, elderberry, elm, hazel, hickory, hornbeam, locust, maples, mulberry, oaks, persimmon, pine, poison oak, poplar, salmonberry, sassafras, sumac, sweetbay magnolia, sweetgum, sycamore, thimbleberry, tulip poplar, willow, and winged elm (1,11). Among the annual and perennial broadleaf weeds controlled are: burdock, chicory, curled dock, dandelion, field bindweed, lambsquarters, plantain, ragweed, smartweed, vetch and wild lettuce (1). It is not effective for control of most grasses.

Triclopyr is also recommended for the control of woody and herbaceous weeds in non-crop areas including industrial manufacturing and storage sites, and rights-of-way such as electric power lines, communication lines, pipelines, roadsides and railroads. Triclopyr induces characteristic auxin-type responses in plants (8); i.e., it regulates longitudinal cell structure so as to control bending of the stalk or stem in phototropic responses (12). It is absorbed by both leaves and roots, and is readily translocated through the plant (8). Maximum plant response is achieved when application is made soon after full leaf development (8).

Triclopyr is manufactured by Dow Chemical USA, Ag-Organics Dept. (13). It is produced in two major formulations (8): Garlon 3A and Garlon 4. Garlon 3A contains 44.4 percent active ingredient as the triethylamine (TEA) salt, which is equivalent to 31.8 percent acid equivalent and is present in the formulated product at 3 lbs acid equivalent/gallon. This water-soluble formulation also contains methanol. Garlon 3A is also available as Experimental Herbicide M-3724 in areas where the Garlon 3A label has not been approved (8). Garlon 4 is an oil-soluble water-emulsifiable ethylene glycol butyl ether ester (EGBE) formulation containing 4 lbs of triclopyr acid equivalent/gallon (8). Surfactants may be added to Garlon 3A formulations to improve its effectiveness (1). Water is the usual carrier for foliar sprays; fuel oil is used for basal sprays (14).

2.0 PHYSICAL/CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The active ingredient of triclopyr is 3,5,6-trichloro-2-pyridinyloxy-acetic acid:



It is a white, odorless solid with melting point of 148-150°C. Solubility in various solvents at 25°C is (14):

Solvent	g/ml	Solvent	g/ml
Acetone	98.9	n-hexane	0.041
Acetonitrile	12.6	n-octanol	30.7
Benzene	2.73	Xylene	2.79
Chloroform	2.73	Water	0.043

Vapor pressure data are shown below as a function of temperature (14):

Temperature	mm Hg
25	1.26×10^{-6}
40	5.30×10^{-6}
50	1.03×10^{-5}
70	1.04×10^{-4}

3.0 ENVIRONMENTAL FATE

Being a very new pesticide, the fate of triclopyr in the environment (especially the forest environment) following application has not been the subject of much scientific investigation. The very limited data which have been reported are from studies performed or sponsored by the manufacturers and pertain to non-forest environments.

3.1 UPTAKE AND METABOLISM BY PLANTS

Limited studies have been conducted on the uptake of triclopyr by plants. As noted previously, it induces auxin-type responses in plants. It is adsorbed by both leaves and roots, and is readily translocated throughout the plant (8).

The effects of photoperiod and temperature on the translocation of triclopyr were studied by Radosevich and Bayer (15) on tanoak, snowbrush ceanothus, bigleaf maple, beans and barley. Translocation of triclopyr was observed to be greatest under warm temperatures and long-day photoperiods. With colder temperatures and short-day photoperiods, movement was greatly reduced. Following application directly to leaves, triclopyr was observed to move readily in the symplasts, with the preponderance remaining in the shoot. Applications to the roots resulted in very little apoplastic mobility. In a subsequent study on absorption of triclopyr by tanoak, greater amounts were absorbed by immature leaves than mature leaves and by abaxial surfaces containing large stomatal densities than by axial surfaces (16).

No data are available on the metabolic degradation (if any) of triclopyr in plants.

3.2 FATE IN SOIL

In general the fate of a pesticide in soil can be described in terms of six factors: volatilization, photodecomposition, adsorption/leaching, runoff, and chemical and microbial degradation. Although actual field data are unavailable, volatilization is not considered to be a significant contributor to the loss of triclopyr following application because of the very low volatility of triclopyr (see Section 2.0). No data are available on the photodegradation (if any) of triclopyr in soil. However, based on photodegradation data for water (see Section 3.3), it is likely that photodegradation of triclopyr may occur in soil and from foliar surfaces. The adsorption/leaching and degradation data which have been submitted by Dow to EPA in support of registration applications for various uses of triclopyr are discussed in the following sections.

3.2.1 Adsorption, Leaching and Runoff

Triclopyr is considered a mobile herbicide (9). It is rapidly and reversibly adsorbed on soil particles. The extent of adsorption is primarily a function of soil type. Soil organic matter is the principal soil parameter responsible for adsorption, with increasing soil organic matter resulting in increased adsorption (9). Several laboratory studies have been conducted on the adsorption of the ^{14}C labelled triethylamine salt of triclopyr by 12 soils (17). The organic carbon content of the soils ranged from 0.081 percent to 21.7 percent. Adsorption coefficients K_d and K_{oc} were measured and ranged from 0.016 to 14.5, and 12 to 78, respectively, indicating mobility. In a study using 3 soil types, the principal degradation product of triclopyr (trichloropyridinol) was found to have K_d and K_{oc} adsorption coefficients of 0.63 to 5.64 and 114 to 156, respectively, indicating low-to-intermediate mobility (18). No quantitative data are available on the effects of pH on triclopyr adsorption; because of its weakly acidic character, however, adsorption is expected to be favored under acidic conditions.

The adsorption capacity of a given soil type affects the potential for leaching of the herbicide from soil. Based on available limited data, it appears that triclopyr is leachable but that leaching should be less pronounced in soils with high organic matter content than in soils with lower organic matter content. Results of a leaching study using a low organic matter content soil (loam sand, 0.62 percent organic carbon) leached with 0.5 inches of water per day for 45 days showed that 75 percent to 80 percent of the triclopyr leached through the 12-inch soil column between days 11-15 (19). The trichloropyridinol degradate was found to be significantly less leachable; while the triclopyr moved through the column after about 7.5 inches of water were applied, the degradate required 13 inches of applied water to completely pass through the column. In a study of 6 soils under test plot field condition in 6 states, small amounts of triclopyr and its degradates were observed in the 6-12 inch and 12-18 inch soil layers between 28 and 56 days following application of Garlon 3A at a rate of 3 gallons/ acre and normal rainfall conditions (20). The trichloropyridinol degradate was less leachable and showed maximum residues in the 0 to 6 inch soil layer between 28 and 56 days after application and declined thereafter. The trichloromethoxy pyridine degradate remained around 0.1 ppm or less at all sample intervals. The six soil types tested were Tiffon, Georgia loamy sand; Fargo, ND clay; Corvallis, or hazelaire comples; Benchley, TX clay to clay loam; Arthurdale, WV unspecified soil; and Laramie, WY Forelli fine sandy loam.

Because of its mobility and rapid desorption from soil particles, some loss of triclopyr due to solubilization and/or runoff may be expected following field application after rainfall. This was confirmed by results of several small-scale water monitoring programs in which residues of 6 ppb were observed in runoff water 5 months after application and 1 ppb was observed 9 months after application of 3 lb/acre triclopyr as the triethylamine salt, and after 150 cm of natural rainfall (21).

3.2.2 Chemical and Microbial Degradation

Triclopyr is not considered a persistent compound in soils. Laboratory studies have shown that triclopyr is decomposed quickly by soil microorganisms (9,14). Microbial degradation results in the formation of 3,5,6-trichloro-2-pyridinol and trichloromethoxypyridine (9,22). The average half-life in soil is 46 days with the actual value dependent on soil type and climatic conditions (14). Studies on the aerobic soil degradation of radio-labelled triclopyr indicated degradation to trichloro-2-pyridinol with a half-life between 79 and 156 days at 15°C, and less than 50 days at 25-35°C (9,22,23). The trichloro-2-pyridinol subsequently degraded to trichloromethoxypyridine, and eventually to CO_2 with 7 to 30 percent evolution of CO_2 at 375 days. Half-lives of these secondary reaction products and the degradation mechanisms have not been determined. The microbial degradation of triclopyr was shown to be approximately 5 to 8 times slower under anaerobic conditions (i.e., waterlogging) than under aerobic conditions in a study using Illinois silty clay loam and Mississippi silt loam at 25°C (24).

Trichloropyridinol degradation has been shown to yield mostly carbon dioxide and some trichloromethoxypyridine (25). Tests with 15 soils from 10 major agricultural areas have indicated a half-life of 8 to 279 days for trichloropyridinol. Twelve of the 15 soils showed half-lives of less than 90 days. Two unidentified degradates were found at 1.8 to 6.5 percent of the initial radiolabelled trichloropyridinol. When the other degradate of triclopyr, trichloromethoxypyridine, was studied, results showed extensive degradation to carbon dioxide with estimated half-life of 50 days in two soils (Commerce silt loam and Flanagan silty clay loam), but more than 300 days in another soil (Yoho loam) (26). Trichloropyridinol was also found as a degradate of trichloromethoxypyridine.

In a study by Norris, et al. (27) of the fate of triclopyr on small hillside pastures in southwestern Oregon applied at a rate of 3.36 kg/ha, triclopyr residues were 350, 172, and 65 ppb at 6, 9, and 12 months after application, respectively.

Degradation of triclopyr in soil does not occur to any appreciable extent via chemical hydrolysis or other chemical routes (9). Laboratory studies using a silt loam soil have indicated that triclopyr does not degrade in sterile soil, but does degrade rapidly in the same soil when it is not sterilized (28).

3.3 PERSISTENCE IN WATER

Several laboratory studies conducted on the persistence and degradation of triclopyr in water have indicated triclopyr is stable to hydrolysis in buffered solutions for periods up to 9 months at pH 5, 7, and 8 and at 15, 25, and 35°C (29). Several photodegradation products, including 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine, were formed in minor amounts (less than one percent). Chemical hydrolysis is thus not expected to be a major pathway of triclopyr degradation in the aqueous environment.

The rate of triclopyr photodegradation in water is rapid in both natural sunlight and in the laboratory; half-life is 10 hours in water at 25°C (14, 30). The first degradation product is trichloropyridinol, which is rapidly degraded to various pyridine polyols formed via photolytic hydrolysis of the ring chlorine atoms (30). These primary and secondary photoproducts are further degraded in the aquatic environment. Thus, photodegradation is a major pathway for the dissipation of triclopyr in aquatic environments.

4.0 IMPACTS ON NON-TARGET PLANTS AND ORGANISMS

At high application rates, triclopyr can cause injury to conifers and is not generally recommended for conifer release. In a study of the aerial applications of triclopyr and other herbicides in spruce-fir forests of Maine (31), Garlon 3A applied at a rate of 4.4 kg/ha caused minor injury to a small percentage of conifers, but at a rate of 2.2 kg/ha caused no injury. Injury to conifers following triclopyr applications have also been reported in the Pacific Northwest and in Sweden (5,32).

Triclopyr also exhibits some toxicity to agricultural crops, depending on application rates. Triclopyr applied at a rate of 0.5 lb a.i./acre showed some inhibition of cucumber yields over periods of at least 3 months following application, while rates of 3.0 and 9.0 lbs a.i./acre showed 50 percent inhibition of cucumber yields after a period of at least 4 months (33). Triclopyr applied at a rate of 0.5 and 1 ounce acid equivalents/acre had very little noticeable effect on wheat and no noticeable effect in bean stands planted 3, 8, 12, and 17 weeks after treatment (9). In general, most broadleaf crops will tolerate small quantities of triclopyr to a greater extent than other auxin-type herbicides (14).

Since triclopyr is rapidly degraded by soil microorganisms, there would not be sufficient residue carryover to cause injury to susceptible species in the next growing season (8).

4.1 FISH

Both triclopyr and the amine salt formulation Garlon 3A have very low toxicity to fish and lower aquatic organisms (see Table 1). No data are available on the fate and degradation products of triclopyr in fish or lower aquatic organisms.

TABLE 1. AQUATIC TOXICITY (96-HR AND 48-HR LC_{50}'s) OF TRICLOPYR AND GARLON 3A (8,14)

Species	Exposure	Triclopyr	Garlon 3A
Bluegill	96 hr	148 ppm	891 ppm
Rainbow trout	96 hr	117 ppm	552 ppm
Oysters	48 hr	---	56-87 ppm
Shrimp	96 hr	---	895 ppm
Crab	96 hr	---	>1,000 ppm

4.2 ANIMALS

Based on tests with laboratory animals, both triclopyr and its formulations are considered to have low toxicities to warm-blooded animals (see Table 2).

TABLE 2. ACUTE TOXICITY (ORAL LD_{50} AND LC_{50}) OF TRICLOPYR AND ITS FORMULATIONS TO LABORATORY ANIMALS (8,14,34)

Species	Triclopyr	Garlon 3A	Garlon 4
LD_{50}			
Rat (female)	630 mg/kg	2,140 mg/kg	2,140 mg/kg
Rat (male)	729 mg/kg	2,830 mg/kg	2,460 mg/kg
Rabbit (mixed)	550 mg/kg	---	---
Guinea pig	310 mg/kg	---	---
LC_{50}			
Mallard duck	>5,000 ppm	>10,000 ppm	>10,000 ppm
Japanese quail	3,278 ppm	---	---
Bobwhite quail	---	11,622 ppm	9,026 ppm

Dosages of triclopyr of 30 mg/kg/day produced no carcinogenic effects in mice and rats (34). Triclopyr was found to be non-mutagenic in dominant lethal and host mediated assay tests (34). It is considered mildly fetotoxic, exhibiting a reproductive toxicity effect at 200 mg/kg/day (34).

No data are available on the insecticidal activity of triclopyr on beneficial insects.

4.3 SOIL MICROORGANISMS

Triclopyr is non-toxic to soil microorganisms. In a laboratory study of the effect of 500 ppm of triclopyr on 6 soil microorganisms (*Aerobacter aerogenes*, *Pseudomonas aeruginosa*, *Salmonella typhosa*, *Staphylococcus aureus*, *Aspergillus terreus*, and *Pullularia pullulams*), growth of the microorganisms was compared to controls (35). After 72 hours of incubation, no apparent effect was observed. The results of laboratory and field studies by Hallborn and Bergman (36) showed that treatment of *Peltigera praetextata* lichen and its free-living pshycobiant algae *Nostoc sp.* with Garlon 3A at rates typically used in forestry applications did not significantly affect the rates of nitrogen fixation by either organism.

4.5 BIOACCUMULATION

Triclopyr and its degradates trichloropyridinol and trichloromethoxypyridine do not accumulate to any appreciable extent in fish. Several laboratory studies have indicated that these compounds do not accumulate in edible portions of catfish or in fish heads, viscera or skins (37). Mosquito fish also do not accumulate significant residues of trichloropyridinol (37).

No data are available on the bioaccumulation of triclopyr in animals or microorganisms.

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II. INSECTICIDES

Common Name:	Acephate
Chemical Name:	O,S-dimethyl acetylphosphoramidothioate
Major Trade Names:	Orthene; Ortran; RE 12,420; Ortho 12,420; Ent 27822
Major Applications in Forestry:	Control of spruce budworm and gypsy moth

SUMMARY

Acephate is an organophosphate broad spectrum insecticide utilized in forestry primarily for the control of spruce budworm and gypsy moth. Acephate is a neurotoxin which kills insects both on contact and through systemic action on chewing and sucking insect species.

The major pathways for removal of acephate from the environment are uptake in plants, metabolism in soil, and leaching. Acephate does not appear to photodegrade.

Acephate is taken up by plants through the foliage and roots and is translocated throughout the plant. Within the plant, 5 to 10 percent of the acephate is metabolized to Monitor, a considerably more toxic insecticide than acephate. The remaining acephate degrades into innocuous salts.

Acephate and Monitor are readily leached in soil. Acephate is also rapidly degraded in soil, primarily by soil microorganisms. Half-lives range from 0.5 to 13 days. Degradation of acephate in water is slower than in soil. At 21°C and pH 7, acephate has a half-life in water of 46 days. The rate of hydrolysis is higher with increasing temperature and pH.

Acephate is not expected to cause significant mortality in birds when applied at recommended rates. However, brain cholinesterase inhibition has been observed in exposed birds. Acephate has low toxicity to fish (96-hr TL_{50} for trout, bluegills, catfish is >1000 ppm) although it may temporarily alter feeding habits. Non-target insect populations may decrease after exposure to acephate and acephate is highly toxic to bees (LD_{50} of 1.20 µg/bee). It is considered to be of low toxicity to mammals. Based on acute toxicity data, Monitor is considerably more toxic than acephate (oral rat LD_{50} of 7.5 mg/kg for Monitor vs. 700 mg/kg for acephate).

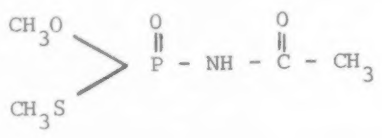
1.0 INTRODUCTION

Acephate is an organophosphate broad spectrum insecticide manufactured by Chevron Chemical Company, Ortho Division, and marketed as Orthene. It has been registered for commercial use on ornamentals, lawns, and non-crop bearing trees and has since been registered for use on cotton, beans, celery, head lettuce and sweet peppers to control a number of agricultural pests (1). In commercial forestry, acephate is used both in seed orchards and in forests. In seed orchards, Orthene "Tree and Ornamental Spray" is applied by ground spray rigs at a rate of 2/3 lb/100 gal water/acre. It is used on conifer seed orchards to control Douglas-fir coneworm, gall midge, and other cone and seed insects (2). In forests, Orthene "Forest Spray" is aerially applied at a rate of 2/3 to 1-1/3 lbs in 1 gallon/acre on stands of white fir and other conifers to control western spruce budworm and Modoc budworm (2). Orthene "Forest Spray" is also used at a rate of 1/2 to 3/4 lb a.i./acre for control of gypsy moth larvae (1), and it has been used to a limited extent against the spruce budworm in Maine (3).

Acephate is neurotoxic to insects and other animals including man. Its mode of action is the inhibition of acetylcholinesterase, the enzyme that breaks down the neurotransmitter acetylcholine. Acephate kills insects on contact and also passes from leaf surfaces into plant tissue where it gives some systemic protection against chewing or sucking insects for approximately one week (4).

2.0 PHYSICAL/CHEMICAL PROPERTIES

Acephate, O,S-dimethyl acetylphosphoramidothioate, has the following structure:



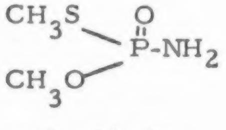
It is a white crystalline solid when pure and is off-white in the technical grade. It has a very low vapor pressure of 2×10^{-6} mm Hg at 25°C. It is highly soluble in water (65 percent) and in polar organic solvents (e.g., 25 percent solubility in methanol), and is slightly soluble in non-polar organic solvents (e.g., one percent solubility in benzene and 0.01 percent solubility in hexane) (5). The melting point of pure acephate is 92-93°C and that of the technical grade is 82-89°C. Acephate is stable at 21°C but decomposes at its melting point. In normal usage and storage, it is not corrosive (4). Insecticide formulations of acephate contain 75 percent active ingredient (5).

3.0 ENVIRONMENTAL FATE

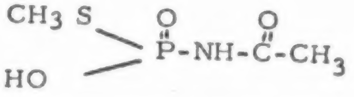
The major pathways for removal of acephate from the environment are uptake in plants, metabolism in soil, and leaching. Acephate does not appear to photodegrade to an appreciable extent on surfaces or in water (5). Most of the breakdown products of acephate appear to have little or no toxicity. However, one breakdown product, methamidophos (Monitor) is a registered pesticide with toxicity and environmental persistence that is largely similar to that of acephate.

3.1 FATE IN PLANTS

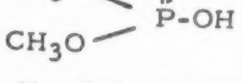
Acephate penetrates plant tissues quickly, within 24 hours (4). Experiments on cotton plants indicate that greater than 80 percent of the acephate applied disappeared from leaf surfaces within 24 hours; more than 50 percent of the applied dose was recovered inside the plant after 24 hours (6). Unabsorbed residues were essentially depleted in 48 hours. A small amount of the absorbed acephate (about 9 percent of the dose) was metabolized to the toxic insecticide, methamidophos, while less than 5 percent of the dose was metabolized to at least four other products. Two of these were identified as O,S-dimethylphosphorothioate and S-methyl acetylphosphoramidothioate which are non-toxic. The structures of these compounds are as follows:



methamidophos
(Monitor)



S-methyl acetylphosphoramidothioate



O,S-dimethyl phosphorothioate

Residues on plant foliage are generally undetectable 70 to 75 days after application. When acephate was aerially applied in New York for gypsy moth control at rates of 0.78 and 0.56 kg a.i. per ha, the average residues of Orthene in leaves after 24 hours were 30.8 and 11.1 ppm, respectively (7). Residues were 0.21 ppm for the 0.78 kg/ha application rate 18 days after spraying and were undetectable (0.02 ppm) within 75 days. Residues from the 0.56 kg/ha application rate were undetectable 20 days after spraying. Devine (7) also reported an average residue in litter of 5.5 ppm one day after aerial application in Pennsylvania of 0.56 kg a.i./ha for gypsy moth control. Twenty days after spraying, residues decreased to 0.03 ppm and were undetectable after 70 days.

Szeto, et al. (8) found that acephate residues could no longer be detected in Douglas-fir needles or in forest litter 60 days following application of 1.12 kg/ha.

Half-lives of about 10 days have been reported for acephate and methamidophos in the rinds of various citrus plants sprayed with acephate (9). Maximum penetration of residues in rind and pulp occurred within 7 days after spraying.

3.2 FATE IN SOIL

Acephate in soil can be readily leached. In one experiment, an amount of water equivalent to 10 inches of rainfall was passed through acephate-containing soil columns. In six tests with different soil types, this quantity of water eluted from 62 percent to 100 percent of the acephate (1). The smallest amount of leaching was in a muck soil with high organic content and the highest values were in sandy soil. In separate experiments (1), the rate of acephate movement through soil relative to the rate of water movement was measured. These relative rates, called R_f values, were between 0.5 and 1.0 for the six soil types. Furthermore, R_f values for methamidophos were not significantly different from those of acephate. Therefore, neither acephate nor methamidophos are tightly bound to soil to a significant extent, and both are capable of rapid leaching from soil.

Acephate is rapidly degraded in soil. Half-lives of acephate at 1 to 10 ppm initial concentration levels in 9 different soil types have been reported to vary from 0.5 to 13 days (see Table 1) with the longest persistence corresponding to a high organic muck soil (1,5). These data are from laboratory experiments conducted under aerobic conditions with the soils wetted to about field capacity.

TABLE 1. THE DEGRADATION OF ACEPHATE IN SOIL (5)

Soil Origin	Soil Type	Half-life (Days)	
		1 ppm	10 ppm
Clarkesburg, Ca.	Clay	1-1/2	1-1/2
Fresno, Ca.	Loam	1-1/2	3
Kettleman City, Ca.	Clay (high pH)	1/2	1/2
Ocoee, Florida	Loamy Sand	1	1
Mt. Holly, N.J.	Sandy Clay Loam	1/2	1
Norwalk, Iowa	Silty Clay Loam	---	2
Greenville, Mississippi	Clay (low pH)	---	1-1/2
Ocoee, Florida	Muck	6	13
Riverside, Ca.	Loamy Sand	---	4*

*20 ppm fortification.

Monitor, the potentially toxic metabolite of acephate is also degraded in soil and has a half-life range of 2 to 6 days based on Chevron studies. Both acephate and Monitor degrade more rapidly in wet soil than in dry soil (5).

The decomposition of both acephate and Monitor in soil is primarily due to the action of soil microorganisms. Figure 1 shows the relative rates of decomposition of acephate in two different soil types under sterile and non-sterile (natural) conditions. As shown in this figure, essentially little or no acephate decomposition takes place in the sterile soil.

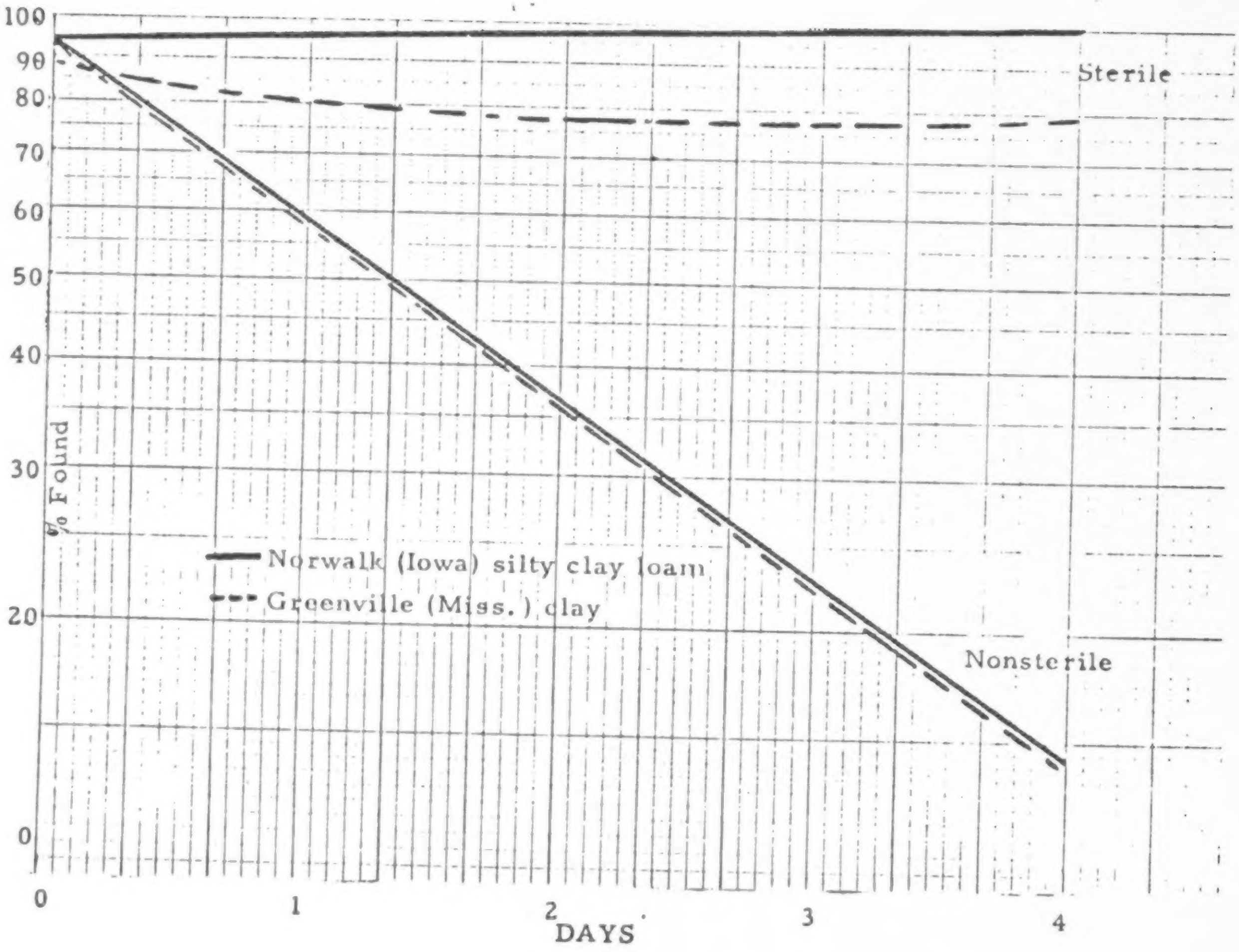
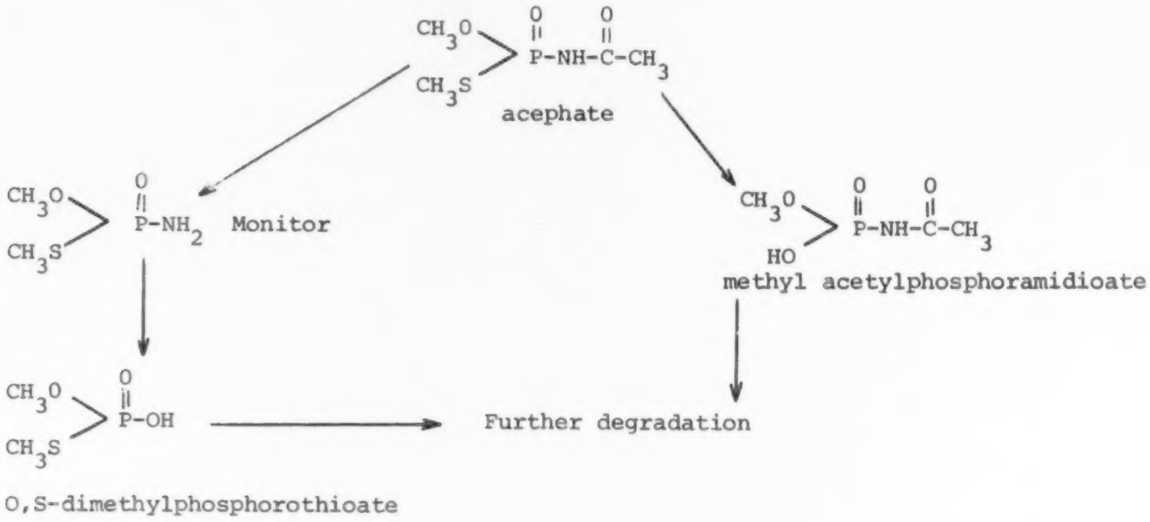


Figure 1. Rates of Decomposition of Acephate in Sterile and Non-sterile Soils (5)

The following routes have been postulated for the degradation of acephate in soil (5):


acephate
Monitor
methyl acetylphosphoramidioate
Further degradation
O,S-dimethylphosphorothioate

3.3 PERSISTENCE IN WATER

While acephate degrades rapidly in soil, its breakdown (hydrolysis) rate in water is relatively slow. The rate is dependent upon pH and temperature (see Table 2) and is higher at higher temperature and pH levels.

TABLE 2. HALF-LIVES (IN DAYS) FOR ACEPHATE AND MONITOR IN WATER AS A FUNCTION OF TEMPERATURE AND pH (5)

pH	Acephate 21°C	Acephate 40°C	Monitor 21°C	Monitor 40°C
3	65.5	29.4	22.0	8.4
5	55.2	29.7	107.8	45.1
7	46.4	16.5	44.0	9.8
9	16.1	2.5	9.2	4.8

Acephate appears to be more susceptible to hydrolysis at high pH. In a recent study, Szeto, et al. (10) studied the hydrolysis of acephate in buffered distilled water over a pH range of 4.0 to 8.2 and incubated for 20 days at 20°C and 30°C. Their results are summarized in Table 3. They found that acephate was quite resistant to hydrolysis between pH 4.0 and 6.9 regardless of temperature; over 80 percent of the acephate was recovered in this range, with greater recoveries at the lower pH. At pH 8.2, however, temperature strongly affected hydrolysis - 78 percent was recovered at 20°C whereas only 18 percent was recovered at 30°C. Higher amounts of monitor were also detected at higher pH. The maximum level of Monitor was found at pH 8.2 and 20°C. However, only 4.5 percent of the acephate added was converted to Monitor.

TABLE 3. THE EFFECT OF pH ON THE HYDROLYSIS OF ACEPHATE IN BUFFERED, DISTILLED WATER, HELD AT 20°C AND 30°C FOR 20 DAYS (10)

pH	Acephate Recovered (μg) $\bar{X}$	± SD*	Monitor Recovered (μg) $\bar{X}$	± SD*	Recovery in % of Acephate Added Acephate	Monitor
			20°C			
4.0	978	20.8	T[†]		97.8	0.2
5.0	927	15.5	T		92.7	0.2
5.6	882	17.5	T		88.2	0.2
6.0	861	16.1	T		86.1	0.2
6.9	842	15.5	10.0	0.4	84.2	1.0
8.2	779	8.5	44.6	0.5	77.9	4.5
			30°C			
4.0	955	21.0	4.9	0.2	95.5	0.5
5.0	902	18.8	T		90.2	0.2
5.6	838	15.0	T		83.8	0.2
6.0	830	14.1	T		83.0	0.2
6.9	825	6.9	16.7	1.9	82.5	1.7
8.2	178	13.0	43.3	2.9	17.8	4.3

*N = 4

[†] T (Trace) < 4 μg

Szeto, et al. (10) also studied the persistence of acephate in water samples from two natural sources, pond water and creek water. The samples were held at 9°C for 42 and 50 days, respectively. The results are presented in Tables 4 and 5. About 83 percent of the acephate was recovered from pond water after 42 days while 45 percent was recovered from creek water after 50 days. Rates of degradation increased greatly when sediments were included in the samples. In the presence of sediments, only 15 percent of the acephate was recovered from pond water (Table 6) and 25 percent from creek water (Table 7). Autoclaving creek water prior to incubation with acephate showed that a major factor in the disappearance of acephate was microbial breakdown of acephate. In creek water without sediments, autoclaving increased acephate recovery by over 30 percent; in creek water with sediments, autoclaving more than doubled the recovery of acephate. Only quantitatively insignificant amounts of Monitor were found in the samples.

Acephate was not found to escape into the atmosphere from the water during any of the experiments.

TABLE 4. THE FATE OF 1 PPM ACEPHATE IN POND WATER AT 9°C[*] (10)

Time, Days	Recovery in % of Acephate Added	
	Acephate	Monitor
0	90.2	ND[†]
0	90.3	ND
2	96.7	0.3
2	94.0	0.8
7	86.7	0.5
7	88.7	0.4
14	86.7	0.7
14	87.3	0.7
21	85.3	0.5
21	84.7	0.6
42	78.0	1.0
42	83.3	1.3

[*] pH was 7.5 at day 0 and had changed to 8.0.

[†] Non-detectable.

TABLE 5. THE FATE OF 1 PPM ACEPHATE IN CREEK WATER AT 9°C, AND THE EFFECT OF AUTOCLAVING* (10)

Time, Days	Recovery in % of Acephate Added	
	Acephate	Monitor
0	95.5	ND†
0	89.8	ND
	Not Autoclaved	
7	80.9	0.4
7	74.3	0.3
21	88.7	0.3
21	87.3	0.4
34	59.8	0.3
34	57.0	0.3
50	45.0	0.4
50	45.5	0.3
	Autoclaved	
43	75.0	0.4
43	76.5	0.4
50	76.8	0.5
50	76.0	0.5

[*] In samples not autoclaved, pH was 7.0 at day 0; after 50 days it had changed to 7.2 with acephate. In autoclaved samples, pH was 7.0 at day 0 and remained unchanged.

[†] ND = Not-detectable.

TABLE 6. THE FATE OF 1 PPM ACEPHATE IN POND WATER AT 9°C
IN THE PRESENCE OF BOTTOM SEDIMENTS[*] (10)

Time, Days	Recovery in % of Acephate Added			
	Acephate		Monitor	
	Water	B.S.[†]	Water	B.S.
0	90.2	ND[‡]	ND	ND
0	89.3	ND	ND	ND
2	56.3	19.5	0.6	0.3
2	58.7	20.7	0.8	0.3
7	42.9	21.3	1.0	0.4
7	50.0	18.2	1.3	0.4
14	37.8	22.4	0.7	0.4
14	39.7	20.5	0.9	0.4
21	31.3	21.6	0.4	0.3
21	33.7	17.5	0.5	0.3
42	17.8	5.7	0.2	0.07
42	15.0	3.9	0.2	0.07

[*] pH was 7.5 at day 0 and had changed to 7.9 with both treatments after 42 days.

[†] B.S. - Bottom sediment.

[‡] ND - Not-detectable.

Based on Chevron data (5), the major hydrolysis product of acephate is O,S-dimethylphophorothioate (II, see diagram). In the physiological pH range, Monitor is not formed. At the extreme pH of 3 and 9, traces of Monitor may be formed. However, it is itself hydrolyzed to II, which is stable under acid conditions, but degrades under alkaline conditions. At pH 7, S-methyl-acetyl-phosphoroamidothioate (III) is also formed. The hydrolytic degradation route for acephate can be shown by the following diagram (5):

TABLE 7. THE FATE OF 1 PPM ACEPHATE IN CREEK WATER AT 9°C IN THE PRESENCE OF BOTTOM SEDIMENTS, AND THE EFFECT OF AUTOCLAVING* (10)

Time, Days	Recovery in % of Acephate Added			
	Acephate		Monitor	
	Water	B.S.†	Water	B.S.
0	95.5	ND‡	ND	ND
0	89.8	ND	ND	ND
		Not Autoclaved		
7	36.0	19.2	0.6	0.4
7	38.0	19.1	0.6	0.4
21	27.1	16.2	0.5	0.3
21	31.5	13.3	0.5	0.4
34	36.5	2.1	0.5	0.1
34	34.7	2.1	0.4	0.1
50	25.9	2.5	0.3	0.07
50	25.1	2.1	0.4	0.07
		Autoclaved		
43	54.0	9.7	0.4	0.2
43	52.0	10.3	0.4	0.1
50	56.8	9.2	0.6	0.3
50	53.2	10.2	0.5	0.2

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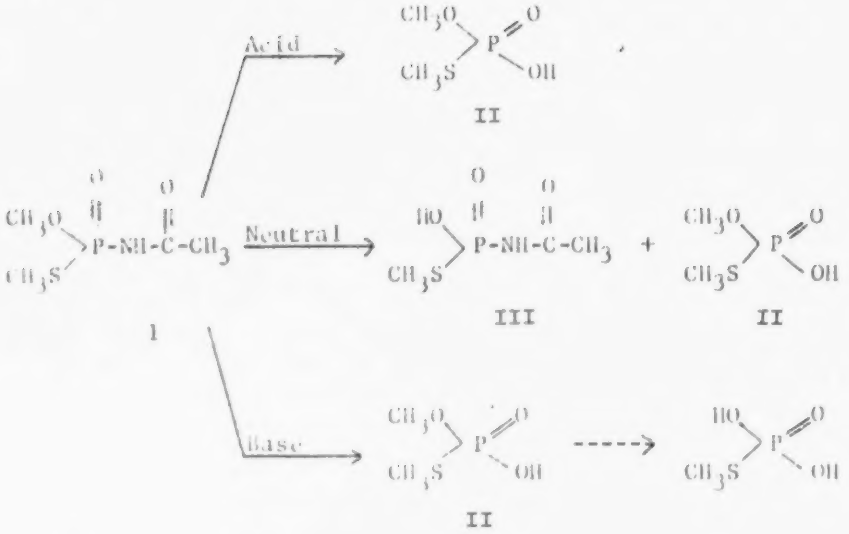
[*] In samples not autoclaved, pH was 7.1 at day 0; after 50 days it had changed to 7.8 with acephate. In autoclaved samples it had changed from 7.1 to 7.3.

[†] B.S. - Bottom sediment.

[‡] ND - Not-detectable.



4.0 IMPACT ON NON-TARGET ORGANISMS

4.1 PLANTS

As noted in Section 3.1, acephate is rapidly picked up and degraded by plants. According to the manufacturer (4), acephate has been demonstrated to be safe to a wide range of plants. Only marginal leaf burns or interveinal chlorosis on elm, crabapple, maple, cottonwood, redbud and weigela has been observed.

4.2 BIRDS

Determination of the effects of Orthene on birds has included observations on population declines, breeding cycles, and bird activity. The effect of acephate on birds in forests sprayed with Orthene at 0.56 and 1.4 kg a.i./ha was studied by Buckner and MacLeod (11). No adverse effects on birds could be attributed to acephate. Population fluctuations were observed but were attributed to other factors. The breeding cycle of birds did not appear to be interrupted.

Further work by Buckner and MacLeod (12) showed that applications of acephate (0.56 kg/ha) combined with Bacillus thuringiensis (19.8 BIU/ha) resulted in reduced warbler activity. However, this impact was considered comparable to normal population and activity changes encountered in untreated environments.

Acephate applied to forested plots at a rate of 0.55 kg a.i./ha was found to cause a decline in song activity of red-eyed vireos (13). There was also a decline in numbers of vireos on treated plots. However, it was uncertain whether acephate affected birds directly or indirectly, by depleting their food supply.

Brain cholinesterase levels have also been studied following forest spraying in an attempt to correlate cholinesterase levels with dosage and bird mortality. Based on the limited amount of data currently available, it appears that brain cholinesterase inhibition of at least 80 percent is required to kill birds with a single oral dose of an organophosphate insecticide, but they may die with only 50 percent inhibition when continuously exposed (14).

An evaluation of the effects of Orthene on songbird brain cholinesterase activity following application of Orthene at 0.5 lb/acre to forest land in Maine showed a significant brain cholinesterase inhibition in evening grosbeaks and magnolia warblers (15). No mortality or evidence of other deleterious effects in songbird populations was found.

Orthene applied to a forest in northeastern Oregon at 1.12 and 2.24 kg/ha caused a 30 to 50 percent inhibition of brain cholinesterase activity in forest birds for up to at least 33 days for 11 of 12 species collected (16). Post spray bird census data suggested that two species of birds may have decreased numbers following spray treatments. One dead grouse was located on the plot treated with 2.24 kg/ha which may be indicative of a greater overall mortality, considering the rapidity with which carcasses disappear due to heat, predators and scavengers. This dose, however, is significantly higher than the doses recommended for forestry use.

LD_{50} data has been reported for a few bird species. The oral LD_{50} for ducks to acephate is 350 mg/kg; for chickens, 852 mg/kg (17). The metabolite, Monitor, is considerably more toxic than acephate - it has an oral LD_{50} for chickens of 25 mg/kg.

4.3 FISH AND AQUATIC ORGANISMS

Available data indicate that acephate is of low toxicity to fish (4). Rabeni and Stanley (18) studied the effects of acephate on fish following aerial spraying in Maine forests. Acephate concentrations in the streams studied reached a maximum of 140 ppb one hour after spraying and residues remained for at least two days. Brook trout, landlocked salmon, longnose sucker, and common sucker were analyzed for brain acetylcholinesterase activity, effects on feeding, and growth. Suckers were the only fish with significant depression of acetylcholinesterase activity (up to 29 percent decrease). Analysis of stomach contents showed that acephate altered feeding habits. Exposed fish consumed more terrestrial prey (beetles, wasps, moths, spiders) than unexposed fish (which preyed primarily on immature aquatic insects). However, these effects were transient. No unusual growth patterns were observed. Also, population densities of benthic invertebrates did not appear to be affected.

Hydorn, et al. (19) also analyzed the stomach content of mature brook trout from sprayed and unsprayed streams for arthropods. The results, shown in Table 8, indicate that within 48 hours after exposure to aerial applications of 0.56 kg/ha acephate, fish consumed many more spiders and other arthropods.

In another study, Orthene was applied at a rate of 0.56 kg a.i./ha to a freshwater pond (20). No long-term adverse effects to the pond and stream ecosystem were observed. No deaths or adverse effects were found in fish or phytoplankton. The only significant population decrease was obtained for midges.

Chevron (4) reports that Orthene's toxicity to fish is extremely low. The 96-hour (TL_{50}) of technical Orthene for trout, bluegills, and catfish is greater than 1000 ppm. Fish continuously exposed to Orthene temporarily accumulate small amounts in body tissues, but Orthene is rapidly eliminated as levels of the chemical in water drop.

4.4 BEES AND OTHER INSECTS

Chevron (4) reports that acephate is highly toxic to bees in treatment areas at the time of application. The mortality of bees reportedly increases immediately after acephate spraying at normal application rates ($\sim$1.0 lb/acre). Nurse bees are particularly affected, with heavy mortality continuing for 2 days and pollen collection curtailed for as long as five days. The

TABLE 8. ABUNDANCE OF SPIDERS BY FAMILY IN STOMACHS OF BROOK TROUT CAPTURED FROM STREAMS IN ACEPHATE-SPRAYED AND UNSPRAYED FOREST (19)

Family	Unsprayed stream			Sprayed stream 1			Sprayed stream 2		
	Prespray 2–6 days	Post-spray 24–48 h	Post-spray 4–8 days	Prespray 2–6 days	Post-spray 24–48 h	Post-spray 4–8 days	Prespray 2–6 days	Post-spray 24–48 h	Post-spray 4–8 days
Agelenidae	0	1	0	0	0	0	0	0	0
Anyphaenidae	0	0	0	0	0	0	0	2	0
Araneidae	0	0	0	0	9	2	0	14	0
Clubionidae	0	0	0	0	6	0	1	10	0
Dictynidae	0	0	0	0	1	1	0	1	0
Hahniidae	0	0	0	0	0	1	3	0	0
Linyphiidae	1	0	0	1	1	2	0	10	0
Lycosidae	0	1	0	0	1	0	2	0	0
Philodromidae	1	2	0	0	6	3	0	3	1
Salticidae	0	0	0	1	3	0	0	7	1
Tetragnathidae	1	0	0	0	26	8	6	41	2
Theridiidae	0	1	0	0	19	1	1	1	0
Mean no. spiders/ fish	0.38	0.45	0.00	0.25	7.20	1.50	1.30	12.71	0.40
(No. fish)	(8)	(11)	(10)	(8)	(10)	(12)	(10)	(7)	(10)

LD_{50} for Orthene has been reported to be 1.20 μg/bee, which is considered to be extremely toxic (21).

Laboratory and field studies conducted by Lake Ontario Environmental Laboratory (22) indicate that several non-target insects are adversely affected after aerial application of acephate at 0.5 lbs/acre. Lepidoptera larvae, Diptera larvae, and Hymenoptera (predominantly Formicidae) were the most sensitive whereas Coleoptera were least affected. Also, there was a knockdown immediately after treatment affecting all orders of arthropods collected. Within one month the populations which were depressed recovered to pretreatment levels and no species were totally eliminated. Hydorn (19) has also observed that caged spiders in an acephate-sprayed forest behave abnormally and have a low survival rate.

4.5 MAMMALS

Acephate is considered to be of very low toxicity to mammals when applied at recommended levels (3,4,10,23). In field tests, Orthene applied at 0.56 kg a.i./ha did not appear to adversely affect small mammals or cause interruption of their breeding cycle (11). Other studies on the effects of Orthene on small mammals also did not detect any significant adverse effects (24). In these studies, mortality, emigration, stomach contents and growth, juvenile to adult age class ratio, incidence of pregnancy and lactation, and other reproductive effects were considered. White-footed mice, short-tailed shrews, and red-backed voles were the primary species analyzed.

Toxicity data for Orthene indicate the oral LD_{50} in rats is 700 mg/kg, while the skin LD_{50} in rabbits is 2000 mg/kg (17). Acephate is also reported to irritate rabbit eyes but the eyes appear normal after two weeks (4). The metabolite, Monitor, is considerably more toxic. Its oral rat LD_{50} is 7.5 mg/kg and the skin LD_{50} in rabbits is 118 mg/kg (17).

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Common Name:	Carbaryl
Chemical Name:	1-naphthyl-N-methylcarbamate
Major Trade Names:	Sevin-4-oil; Sevin 50WP, 80WP, 80S
Major Applications in Forestry:	Used primarily against the defoliating insects, the gypsy moth, spruce budworm, and tussock moth.

SUMMARY

Carbaryl is a widely used broad spectrum insecticide. Forestry applications of 0.75 to two pounds a.i. per acre are used to protect mature trees against defoliating insects such as the gypsy moth, spruce budworm, and tussock moth. Union Carbide is the sole producer of carbaryl in the United States. Most of the carbaryl used in this country is for agriculture. Industrial consumption in 1972 was one million pounds, only 4 percent of total carbaryl consumption. Carbaryl is available in several formulations under the trade name Sevin. The forest industry utilizes Sevin-4-oil and the wettable powders primarily.

Carbaryl is a contact and stomach poison in insects with no systemic effect. Its mode of action is to inhibit acetylcholinesterase. Of the carbamate insecticides, carbaryl has received the widest distribution.

Carbaryl is only slightly soluble in water and has a low vapor pressure. It is stable at room temperature at acid pH but readily hydrolyzes to 1-naphthol, CO_2, and methylamine in alkaline solutions.

Carbaryl is considered "moderately" persistent in the environment. Reported half-lives range from a few days to several months depending on environmental conditions. Degradation is primarily by chemical hydrolysis in water and microbial decomposition in soil.

Carbaryl is also taken up and metabolized by target and non-target insects, plants and animals. Metabolic products include 1-naphthol, methylamine, formaldehyde, ammonia and hydroxylated ring compounds. Conjugates are also formed with body substances. These are primarily glucosides in insects, glucuronides in animals and glycosides in plants.

Most of the carbaryl applied to a forest is deposited on vegetation. Residues on plants are measured as ppm of plant material and as amounts per unit surface area. Reported half-lives calculated from surface residues are 12 to 22 days; reported half-lives based on residues in plant material are only 3 to 8 days.

Few investigations of carbaryl volatilization were found in the literature. Carbaryl would not be expected to be readily volatile because of its low vapor pressure. However, when hydrolysis to 1-naphthol occurs, volatilization of 1-naphthol may be a means of dissipation from leaf surfaces.

The fate of carbaryl in forest soils is determined primarily by the extent of adsorption, chemical hydrolysis, and microbial decomposition. Several field studies have measured carbaryl residues in soil. Results vary from rapid disappearance in a few days to persistence after 16 months. The amount of carbaryl applied, soil type and depth of sampling appear to influence residues in soil over time. Adsorption of carbaryl to soil is reversible and occurs to a greater extent in organic than inorganic soils. Microbial decomposition appears to be a major contributing factor to carbaryl dissipation in soils.

Soil bacteria and fungi have been shown to degrade carbaryl primarily to 1-naphthol and CO_2. Several hydroxylated products and some as yet unidentified compounds are also formed. Soil bacteria and fungi have also been shown to degrade 1-naphthol to some extent even though it is toxic to microorganisms. In most soil degradation studies a portion of the carbaryl added to the system remained in the soil as an unextractable residue. This unextractable residue could not be chemically analyzed but was found to be nontoxic.

Carbaryl enters forest streams primarily by direct application as a consequence of forest spraying. Its persistence in water is dependent on pH and temperature. At alkaline pH, carbaryl is hydrolyzed to 1-naphthol. This process is retarded at low temperatures (e.g., 3°C) and enhanced by higher temperatures (e.g., 28°C). Carbaryl has been shown to undergo photolysis in sunlight under acid conditions. The photolysis rate in water is influenced by the level of dissolved oxygen, pH and amount of incident radiation (shade, time of day, time of year).

Forestry use of carbaryl can be expected in general to affect insect and arthropod populations and the aquatic biota in the treated area. Carbaryl exhibits little phytotoxic effect but has been reported to cause injury to certain plants, especially if rain or high humidity persists after application. Carbaryl does cause fruit to fall from apple trees and has been used for fruit thinning. Carbaryl is toxic to fish but is not retained in muscle tissue. The 96-hour LC_{50}'s range from 1 to 20 ppm; fish are generally even more sensitive to 1-naphthol than to carbaryl. Aquatic organisms are particularly susceptible to the toxic effects of carbaryl in water. The 96-hour LC_{50}'s range from 3 to 10 ppb. The natural animal composition of an experimental estuarine community was disrupted by exposure to only 0.1 ppm carbaryl for 10 weeks.

The effects of carbaryl on forest animals has not been extensively studied. Rodent reproduction has been affected by application rates of about 4.5 lbs/acre. Use of 4.5 lbs/acre decreased small mammal populations. Brain cholinesterase levels have been used to measure the magnitude and extent of exposure of forest birds to carbaryl. The effects of forest spraying on birds has been minimal as determined by measurement of brain cholinesterase activity. Temporary territory abandonment and loss of food supply have been noted. Larger doses will produce decreased growth, abnormal body organs and decreased hatching of eggs.

Carbaryl adversely affects many beneficial insects, especially aquatic insects and honey bees. The high toxicity of carbaryl to honey bees is probably the major hazard to non-target organisms in forest applications. Susceptibility of aquatic arthropods that serve as food for fish is also a problem in forest systems. Small amounts of carbaryl in streams (40 to 80 ppb) will substantially reduce numbers of aquatic insects. Populations of soil arthropods are reduced by application of one to two pounds per acre but generally return to normal the following year. The toxicity of carbaryl to honey bees is extended by the ability of forager bees to collect the powder formulation along with pollen and carry it back to the hive where it can remain toxic for up to 8 months. Carbaryl should not be applied at a time when bees are foraging and hives should be moved out of the area.

Carbaryl has been shown to be toxic to marine and freshwater algae and to reduce litter decomposition. Its hydrolysis product, 1-naphthol, is toxic to certain fungi and bacteria. Bioaccumulation studies show carbaryl does not accumulate in fish or aquatic invertebrates. However, bioaccumulation ratios for algae and duckweed are relatively high. Biomagnification effects on food chains due to large accumulations of carbaryl in organisms of the first trophic level is not known.

A number of issues have been raised regarding the real and potential consequences of carbaryl use in forestry. Some of these issues relate to environmental fate and environmental impacts. Carbaryl readily hydrolyzes to 1-naphthol in the environment. There is some evidence the 1-naphthol is more toxic to certain aquatic organisms than carbaryl. It is possible that effects attributed to carbaryl are actually due to 1-naphthol. Extensive aerial spraying of carbaryl is being questioned as a safe, effective means of insect control. Enhancement of virus production has been demonstrated in laboratory studies. Although carbaryl has been converted to a nitroso derivative in the laboratory, no formation of nitrosamines was found in soil.

1.0 INTRODUCTION

1.1 BACKGROUND

Carbaryl is a broad spectrum insecticide that is widely used in the United States and throughout the world. It is applied to control a variety of insect pests on field crops, forests, rangelands, gardens, poultry and pests (1,2). Carbaryl was developed as a pesticide in 1956 and first registered for agricultural use in 1958. It is currently registered for control of over 545 insects on over 106 different crops in the United States (3). Carbaryl has been presented as a substitute for DDT that is effective against insect pests, relatively non-persistent in the environment and generally of low toxicity to non-target organisms (4,5).

Forest industry uses of carbaryl are primarily to protect mature trees from defoliating insects such as the spruce budworm, gypsy moth and tussock moth. The largest forest aerial pesticide spray program in the United States involves the use of carbaryl against the spruce budworm in northern Maine. In 1980 the plan called for spraying 1.1 million acres of forest land with carbaryl and 200 thousand acres with *Bacillus thuringiensis* at an estimated total cost of $8 million (6). Table 1 lists forestry uses and application rates based on recommendations by the National Forest Products Association, USDA and Union Carbide, the only producer of carbaryl in the United States. The major agricultural crop uses are against pests on corn, soybeans, cotton, fruits and vegetables (1).

United States consumption of carbaryl for 1972 was estimated at about 25 million pounds, 19 million pounds of which were used in agriculture (1). Industrial and commercial use, which would include forestry, totalled one million pounds; government use was 1.5 million pounds; and home and garden use was 3.5 million pounds. By area, industrial and commercial use was 0.2 million pounds in the northeastern states, 0.2 million pounds in the southeastern states and 0.1 million pounds in the northwestern states.

Union Carbide estimated annual plant capacity is 65 million pounds (1). Various formulations are available under the trade name Sevin. Foreign producers market carbaryl worldwide in several formulations under about a dozen trade names. Sevin, the basic U.S. product, is sold as wettable powders, dusts, granules, baits, and sprayable liquids in oil or aqueous suspensions.

TABLE 1. FORESTRY USES AND APPLICATION RATES FOR CARBARYL (2,7,8,9)

Host Tree	Insect	Application Rate
Eastern hardwoods, hemlocks, pine, spruce	Gypsy moth	0.75-1 lb a.i./gal/acre
True fir, Douglas-fir	Western spruce budworm	1 lb a.i. in oil/acre
True fir, spruce	Spruce budworm	0.75-1 lb a.i. in oil/acre
Eastern hardwoods	Fall cankerworm	0.5 lb a.i./gal/acre
Aspen, western hardwoods	Great Basin tent caterpillar	1 lb a.i. in oil/acre
Beech, maples, northern hardwoods, eastern hardwoods	Saddled prominent caterpillar	1 lb a.i./gal/acre
Eastern hardwoods, pine	Bagworm	1 lb a.i. in 100 gal water
Spruce	Spruce needle miner, aphid	1 lb a.i. in 100 gal water
Pine	Mountain pine beetle	4 lbs a.i. in 23 gal water/50 ft^2 bark
	European pine sawfly	1 lb a.i. in 100 gal water
Eastern hardwoods	Birch leaf miner	1 lb a.i. in 100 gal water
	Boxelder bug	1 lb a.i. in 100 gal water
	Eastern tent caterpillar	1 lb a.i. in 100 gal water
Eastern hardwoods, western hardwoods	Forest tent caterpillar	1 lb a.i. in oil/acre
Douglas-fir	Tussock moth	2 lbs a.i./acre

Table 2 lists the names of various formulations and possible uses of Sevin produced by Union Carbide and foreign manufacturers.

TABLE 2. BASIC SEVIN FORMULATIONS AVAILABLE*

Name	Composition	Active Ingredient	Possible Use
Sevin-4-oil	Sevin in oil	49%, 4 lbs/gal.	Forestland (10,12) rangeland pasture agriculture
Sevin 50WP	Wettable powder	50%	Forest agriculture (13) orchards (apple)(14)
Sevin 80WP	Wettable powder	80%	Forest agriculture (cotton)(15) orchards (citrus trees) (16)
Sevin 80S	Sprayable liquid	80%	Forest (17) agriculture
Sevin 85S	Wettable powder	85%	
Sevimol	Sevin in molasses	40%	Agriculture (cotton)(18)
Sevidol	Sevin and BHC	8% Sevin, 8% BHC	Agriculture (rice)(10)
Sevin	Granules dust	5-10%, 2-10, 25-50%	Agriculture (18) agriculture animal husbandry
	baits concentrates	5% 50-97%	animal husbandry

*The composition and percent active ingredient information was obtained from references 1, 2, 3, 10, and 11.

1.2 USES IN FORESTRY AGAINST DEFOLIATING INSECTS

Carbaryl use in forestry to control tree defoliation by the gypsy moth utilizes aerial application or ground application with mistblower or hydraulic spray. Aerial application involves use of one pound a.i. per acre of Sevin-4-oil or Sevin 80S with Pinolene or Chevron sticker for longer residual activity. Ground application uses Sevin 80S with a sticker at two pounds a.i. per acre for the mistblower and one pound a.i. per acre with the hydraulic sprayer (19). The chemical is applied against larvae in early instars and can give a 90 percent kill in one to two days with about 70 percent foliage protection (7). Approximately 42,000 acres of forests, forested recreation areas and forested communities in Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, and Pennsylvania were sprayed with Sevin in 1979 for gypsy moth control at a cost of about $7 per acre. Most of the areas were sprayed only once. Carbaryl has been used for control of the Douglas-fir tussock moth in northwest forests (4,20). Usually Sevin-4-oil at one to two pounds a.i. per acre is aerially applied. The chemical is directed against the larval state at early instars. One pound a.i. per acre of carbaryl can give 72 to 83 percent mortality; two pounds a.i. per acre can give up to 97 percent mortality in 14 days with measurable foliage protection (4). Application of two pounds a.i. per acre to forests in Montana and Idaho in 1976 by the U.S. Forest Service decreased populations of the tussock moth to the extent that post-treatment egg masses were not in sufficient quantity to repopulate these forests the next year.

The eastern spruce budworm has been a pest of northeastern forests, especially Maine (24). The western spruce budworm has been a problem in western and Rocky Mountain states (25,26). Spruce budworm control in forested areas of these states is usually by means of aerial application of Sevin-4-oil at about one pound a.i. per acre. Almost 2.5 million acres in Maine were treated with carbaryl for spruce budworm control in 1979 (24). More than 8.2 million acres in Maine were treated with carbaryl from 1975 to 1979. Carbaryl has been the primary insecticide since 1975 and the termination of use of DDT. About 78 percent of the treated area in Maine was sprayed with carbaryl. The reasons for heavy use of carbaryl were its low cost and consistent effectiveness (24).

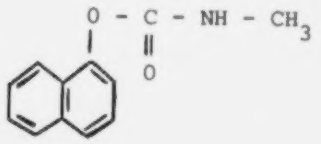
1.3 MODE OF ACTION

Carbaryl is a contact and stomach poison in insects with no systemic effect. Its mode of action is that of a nerve poison in inhibiting acetylcholinesterase (1). Acetylcholine is a major chemical mediator in the autonomic and central nervous systems. It facilitates the transfer of nerve impulses across the synapse at nerve junctions and is controlled by the inactivating effect of the hydrolytic enzyme, acetylcholinesterase. The inhibition of this enzyme results in prolonged nerve transmission and uncontrolled nerve activity (27). Death of insect larvae occurs in one or two days following application of carbaryl to forest systems (24).

The inhibition of acetylcholinesterase by carbaryl is reported to be reversible (1,2,24). Short term exposure of organisms to non-lethal doses of carbaryl would not be expected to result in permanent depression of acetylcholinesterase levels; enzyme activity should return to normal sometime after the carbaryl has been metabolized and/or excreted. Acetylcholinesterase inhibition has been used as an indicator of exposure of birds to carbaryl following forest spraying. Zinkl, et al. (28) measured brain cholinesterase activity in birds five days after application of carbaryl to forests in Montana. Richmond, et al. (29) also used brain cholinesterase levels of collected birds to determine the extent and magnitude of exposure to carbaryl sprayed in Oregon forests. In both studies measurement of enzyme levels of 20 percent or more below normal was considered indicative of exposure; 50 percent inhibition was considered diagnostic for cause of death (28,29).

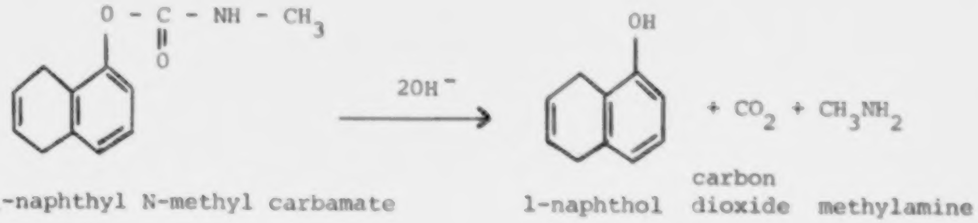
2.0 PHYSICAL AND CHEMICAL PROPERTIES OF THE ACTIVE INGREDIENT

Carbaryl is the common name for 1-naphthyl N-methylcarbamate:



Carbaryl is a member of the carbamate group of pesticides. This group consists of ester derivatives of carbamic acid. Only the esters of N-alkylcarbamic acid have insecticidal activity. In the N-methylcarbamate series, carbaryl has received the widest distribution (11). The technical grade chemical is 99.5 percent + pure. It is a white crystalline solid with a melting point at 142°C (10). It is only slightly soluble in water (40 ppm at 30°C). It is soluble in most polar organic solvents such as acetone and mixed cresols (10). The vapor pressure of carbaryl is very low, 0.002 mm

Hg at 40°C. Its density is 1.232 gm/ml at 20°C (10). At room temperature, carbaryl is nonreactive in acid solution but readily hydrolyzes to CO_2, 1-naphthol and methylamine in alkaline solution:


$O - \underset{\overset{\|}{O}}{C} - NH - CH_3$
$2OH^-$
OH
$+ CO_2 + CH_3NH_2$
1-naphthyl N-methyl carbamate
1-naphthol
carbon dioxide
methylamine

Thus, carbaryl is not compatible with alkaline compounds such as Bordeaux mixture, calcium and barium polysulfides or lime. It is reported by Union Carbide to be stable in light, including ultra violet, unreactive in heat up to 70°C, and stable in a spray formulation under prolonged storage for up to five years (2).

3.0 ENVIRONMENTAL FATE

Carbaryl is taken up and metabolized by insects, plants, and animals exposed by direct application or in the case of insects and animals, by ingestion of contaminated foliage. The persistence of carbaryl in the forest environment is ultimately determined by the extent of volatilization, photodecomposition and chemical and microbial degradation that takes place on plants, in soil and in water. Volatilization following hydrolysis may be important as a means of carbaryl dissipation on foliar surfaces. Chemical hydrolysis and photodecomposition may also occur on leaf surfaces but have been investigated in water and so will be discussed in relation to the fate of carbaryl in water. Microbial degradation is thought to occur primarily in soil and so discussion of fate in soil will emphasize this mechanism.

Carbaryl is considered "moderately" persistent in the environment (30). It contains a readily cleavable carbamoyl group ($> N - \underset{\overset{\|}{O}}{C} -$) and is rapidly hydrolyzed under alkaline conditions (31,32). Reported half-lives range from a few days to several months. Table 3 lists the half-lives of carbaryl under various conditions.

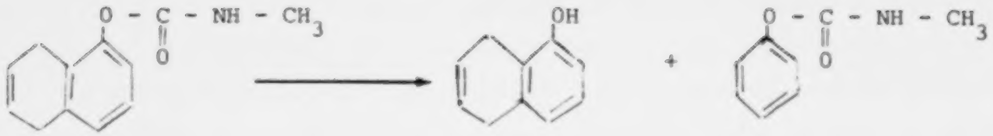
3.1 UPTAKE AND METABOLISM IN INSECTS, PLANTS AND ANIMALS

Carbaryl taken up by target and non-target insects, plants and animals

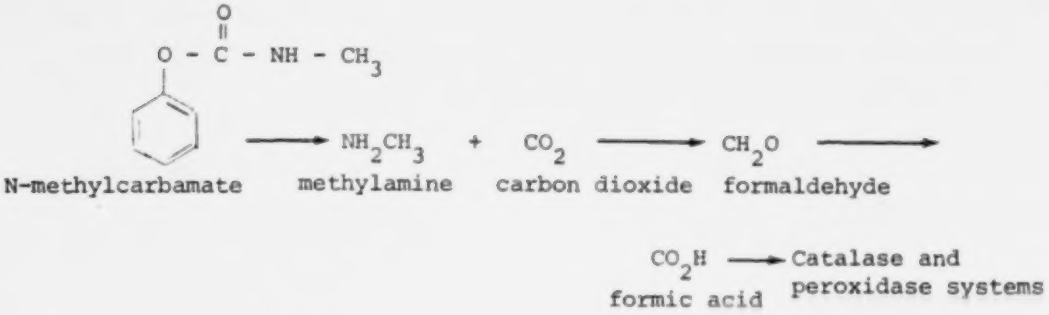
TABLE 3. HALF-LIVES OF CARBARYL FOR VARIOUS ENVIRONMENTAL CONDITIONS

$t_{1/2}$	Environment	Reference
45 hours	Midday sunlight, June, 34°N, distilled water, pH 5.5	33
1.3 days	Water, pH 8	33
4.4 months	Water, pH 6	33
8 days	Grass	12
4.5 days	Douglas-fir	12
38 days	Sea water	34
7-9 days	Soil	2
1-5 days	Water	2
3-4 days	Plant leaves (based on residues in plant material)	2
13 days	Apple leaves (based on residues on leaf surfaces)	14

undergoes metabolic reactions involving both the ring structure and the carbon-nitrogen side chain. Metabolism by target insects is a primary concern in the analysis of the fate of carbaryl in organisms. Plant and animal carbaryl metabolism is also discussed for comparison to insect metabolism. Insects are exposed to carbaryl spray or dust deposited on their bodies and through ingestion of contaminated foliage. Carbaryl is primarily used for control of adult or larval stages of insects (3). Metabolism in insects is exemplified by a study of the larvae of the cotton leaf worm: 1-naphthyl N-methylcarbamate is hydrolyzed to 1-naphthol and N-methylcarbamic acid which is further broken down to carbon dioxide and methylamine. The methylamine is oxidized to formaldehyde and then to formic acid. Further oxidation probably involves the catalase and peroxidase enzyme systems (35). Carbaryl metabolism in the cotton leaf worm is as follows:



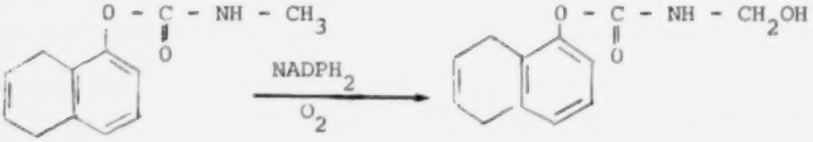
Carbaryl 1-naphthol N-methylcarbamate



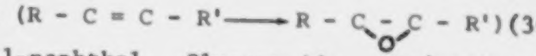
N-methylcarbamate → NH_2CH_3 methylamine + CO_2 carbon dioxide → CH_2O formaldehyde →

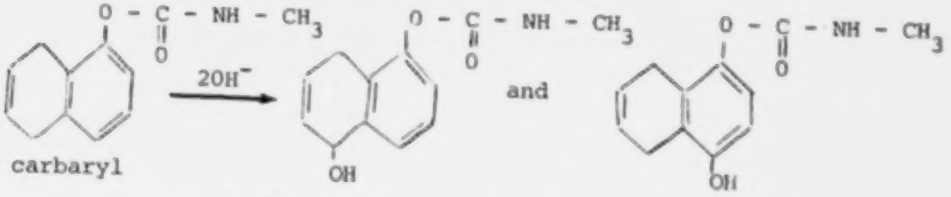
CO_2H formic acid → Catalase and peroxidase systems

Conjugation of carbaryl with insect body substances usually takes the form of glucosides (32). Plants are exposed to carbaryl directly by spray or dust or through uptake from contaminated soil. Metabolism of carbaryl in plants invoves oxidation, hydrolysis, hydroxylation and formation of conjugates with plant constituents, especially carbohydrates. The primary plant-carbaryl conjugates formed are glycosides (36). Oxidation involves the N-methyl group to ultimately form formaldehyde, ammonia and 1-naphthol (11). Hydroxylation of carbaryl in plants is thought to occur prior to conjugation and involves the N-methyl group. There is presently no evidence of hydroxylation of the nitrogen atom (37). An example of carbaryl oxidation in plants is as follows:



carbaryl 1-naphyl N-methylolcarbamate

Although carbaryl is used in animal husbandry as a dust or body wash for insect control, exposure of animals to carbaryl in forest applications is likely to involve ingestion of contaminated foliage or insects. Metabolism of carbaryl in animals results in numerous products from hydrolysis, hydroxylation and epoxidation ( $R - C = C - R' \longrightarrow R - \underset{O}{C - C} - R'$)(36). The primary hydrolysis product is 1-naphthol. Glucuronide conjugates are formed, especially in warm-blooded animals(32), along with sulfates and mercapturic acids.(36). There is a tendency for some metabolites to concentrate in the liver and kidneys of mammals. All animal systems are not alike in their metabolism of carbaryl; for example, the primary metabolic product in man is 1-naphthol, whereas no 1-naphthol is produced in dogs (36). Ring hydroxylation can also occur (11):



carbaryl

5-hydroxy naphthyl N-methylcarbamate

4-hydroxy naphthyl N-methylcarbamate

3.2 PERSISTENCE ON FOLIAR SURFACES

Most of the carbaryl applied to a forest is deposited on vegetation. Persistence of these residues is determined by the extent of volatilization, photodecomposition and chemical degradation of carbaryl, none of which have been measured on foliar surfaces.

3.2.1 Residues on Plants

Several field studies of the persistence of carbaryl on plants have been done primarily because of the use of carbaryl on crops, including edible crops, and because of the reliance on ingestion of treated foliage as a means of exposing target insects to carbaryl in forest applications. The gypsy moth control program in forests of the northeastern United States utilizes 0.75 lbs. a.i. per acre of Sevin-4-oil. Residues have been found on leaves 60 days after treatment. Rainfall is thought to be a major factor in reducing residues (7). A Russian study of a forest application of 0.5 gm. per square meter (4.46 lbs. per acre) reported residues on berries and sprigs of red raspberries, forest strawberries, tree buds and branches one year after treatment (38). Pieper (12) in a field study of carbaryl residues on forest foliage calculated a half life on Douglas-fir of 4.5 days and on aspen of 8 days. Table 4 lists actual residues recovered on various plant types for this study.

TABLE 4. PERSISTENCE OF CARBARYL ON FOREST FOLIAGE TREATED WITH 1 LB A.I. PER ACRE SEVIN-4-OIL (ADAPTED FROM REFERENCE 12)

Foliage Type	$t_{1/2}$ Days	Average Residue Recovered in ppm in Days After Treatment*							
		0 Days	1 Day	3 Days	7 Days	14 Days	28 Days	47 Days	63 Days
Grass	8	70	56	65	46	21	0.3	<0.1	<0.1
Geranium	3	168	99	104	59	24	2.8	0.2	<0.1
Aspen	8	30	30	17	11	17	6.7	2.4	0.5
Douglas-fir	4.5	138	124	44	67	29	4.0	4.5	3.8

*Analytical % recoveries were 89.5% for grass, 86.5% for geranium, 75% for aspen, and 50% for Douglas-fir.

A number of carbaryl plant residue studies have been done for agricultural crops. Measurements of carbaryl residues are in ppm of plant material or μgm per square centimeter of plant surface. Union Carbide reports a half life on plant leaves of 3 to 4 days (2). Table 5 lists some registered uses of carbaryl on crops, allowable residues and measured residues on these crops.

TABLE 5. ALLOWABLE AND ACTUAL CARBARYL RESIDUES ON CROPS (ADAPTED FROM REFERENCE 30)

EPA Registered Use	U.S. Tolerance, ppm	WHO Tolerance, ppm	Residue, ppm	Days After Application	Application Rate
Citrus	10	7	2-8	5	1 lb/100 gal
Cotton	5	1	2-3		2.5 kg/ha
Soybeans	5	1	0.96	38	1-2 lbs/acre
Soybean forage	10		<0.1	85	1-2 lbs/acre

A field study done in India measured residues on bajra plants from a field treated with 13.4,26.8, and 40.2 lbs a.i./acre of granular carbaryl (18). Samples were taken at 15, 30, 60 and 90 days after treatment. No carbaryl residues were detected in bajra plants or grain. The detection limit was <0.07 ppm. Another Indian field study measured residues from four spray applications of carbaryl on cabbage and eggplant at 0.55, 1.1 and 2.2 lb. per acre (13). By the first day after treatment only 55-60% of the carbaryl applied was recovered. After one week only 15-20% of the carbaryl applied was detected. Washing the cabbage prior to residue determination decreased measurements taken the day of application by an average of 95% and measurements taken one day after application by an average of 73% as compared to residues on unwashed cabbage. The half-life calculated for cabbage was 3 days and for eggplant 3.2 days.

Tilden and van Middlelem (39) measured residues on spinach and chicory. Four applications of 1 lb. a.i. per acre resulted in an average residue 8 days after the last application of 3.75 ppm on spinach and 7.1 ppm on chicory. Four applications of 2 lbs. a.i. per acre resulted in an average residue 8 days after the last application of 16.5 ppm on spinach and 18 ppm on chicory. The calculated percent reduction in carbaryl from 1 day to 8 days after treatment are comparable: 1 lb. a.i./acre, spinach 88%, chicory 82% and 2 lb. a.i./acre, spinach 81%, chicory 85%. The rate of dissipation of carbaryl on plants appears to be independent of initial concentration

Sell and Maitlen (14) measured carbaryl residues on the surface of apple leaves from trees treated with an aqueous solution containing 0.5 and 1.0 lb. a.i. per 100 gallons of water. Each test plot consisted of three apple trees which were sprayed until insecticide runoff was produced. Average surface residues on leaves measured 0.70 and 1.71 $\mu gm/cm^2$ the day of treatment. By day 31, the average surface residue had decreased by 90% to 0.07 and 0.18 $\mu gm/cm^2$. The calculated half-life of carbaryl for apple leaves for this study was 13.33 days.

Dislodgeable residues on citrus trees were measured by Iwata et al.(16). Lemon and orange trees were treated with 11.5 lbs. a.i. per acre of Sevin 80WP. Leaves were sampled 5, 10, 15, 30, 45 and 60 days after application. Five days after application surface residues were 5.6 $\mu gm/cm^2$ on orange leaves and 2.4 μgm/cm^2 on lemon leaves. By 60 days after application these residues were reduced by 94% and 83% to 0.36 and 0.41 μgm/cm^2. The fruit was sampled after 52 and 59 days. Pulp residues ranged from <0.01 to 0.02 ppm in oranges and 0.01 to 0.09 ppm in lemons. Half-lives calculated were for orange leaves 14 days and for lemon leaves 22 days.

Depending upon how carbaryl residues in plants have been measured, reported half-life values range from 3 to 22 days. If residues on the surface are determined, half-life values are from 13 to 22 days. Reported half-life values based on residues in plant material are from 3 to 8 days.

3.2.2 Volatilization

Studies of the reduction of carbaryl residues on plant surfaces measure loss of carbaryl by volatilization as well as by decomposition. However, no investigations have been made to determine the relative importance of each mechanism to carbaryl dissipation.

Few investigations of carbaryl volatilization from any medium were found in the literature. Two studies reported losses of carbaryl from surfaces. Over 70% of carbaryl on bean leaf surfaces was dissipated in one day (32). The half-life of carbaryl on glass plates was 14 hours. Metabolites of carbaryl exhibited half lives of 0.3 to 1.8 hours on glass (32). In an analysis for carbaryl and its hydrolysis product, 1-naphthol, on treated apple leaves, only carbaryl could be recovered. The investigators assumed 1-naphthol was formed by carbaryl hydrolysis on the alkaline leaf surface but rapidly vaporized and so could not be detected (40). Carbaryl itself would not be expected to be readily volatile because of its low vapor pressure. 1-naphthol is volatile in steam (41). Intense sunlight may produce an effective temperature on the leaf surface that would result in 1-naphthol volatilization. In intense sunlight, however, photodecomposition of carbaryl may also occur. It is possible that hydrolysis, volatilization and photodecomposition are all responsible for the loss of carbaryl residues from plant surfaces. Full evaluation of the volatility of carbaryl in the forest environment requires further study.

3.3 FATE IN SOIL

Carbaryl reaches the forest floor directly during application and indirectly through residues on vegetation that falls to the ground. The fate of carbaryl in forest soils is determined primarily by the extent of chemical and/or microbial decomposition. Photodecomposition is probably not of major importance in forest soils because of the physical nature of forest systems. Unlike cultivated fields, forests are characterized by heavy vegetation that allows little sunlight to reach the ground. Forest soils are covered by a layer of forest litter. The degradation of carbaryl in forest soil may be very different from degradation in agricultural soil due to the presence of the overlying forest litter. The influence of forest litter on the persistence of carbaryl in forest soil has not been investigated. Investigations into the fate of carbaryl in soil are limited primarily to measurement of residues and laboratory studies of microbial degradation.

Carbaryl is usually sprayed onto forest trees aerially or with ground equipment. An aerial application of 2 lbs. a.i. per 0.75 gal. per acre of Sevin-4-oil was made to Idaho and Montana forests for control of the Douglas-fir tussock moth (4). In Montana only about 20% of the carbaryl applied, 0.15 gal. per acre, actually reached the forest floor. In Idaho the percentage of carbaryl reaching the forest floor was about 29% or 0.22 gal. per acre (4).

3.3.1 Residues in Soil

Several field studies have measured carbaryl residues in soil over a range of application rates. The results vary from rapid disappearance in a few days to persistence after 16 months. The amount of carbaryl applied, soil type, and depth of sampling appear to influence the residues of carbaryl in soil over time.

Kuhr, et al. (42) report that two applications of 3 lbs a.i. per acre to an orchard soil left no detectable residues 8 days after treatment. The detection limit for this study was 1 ppm; only the top two inches of soil was sampled. Residues decreased 93% from 13.8 ppm the day of application to less than 1 ppm after 8 days.

A field study in India measuring soil persistence associated with heavier application rates of granular carbaryl showed a slower decline in residue levels (18). Reductions in soil residues of 62 to 81% after 15 days and 94-98% after 60 days were measured for application rates of 13.4, 26.8, and 40.2 lbs. a.i. per acre. Residues up to 6.3 ppm were still in the soil after 90 days. Soil samples were taken to a depth of 10 cm. A heavy application of 22.7 lbs. per acre of carbaryl to a sandy loam soil resulted in no residues in the first 20 cm of soil after 4 months (36). The upper 1 meter soil layer, however, retained 6% of the initial carbaryl applied after 16 months. These application rates, however, are many times higher than those in current use. At normal application rates, residues are expected to persist for a shorter period of time. Union Carbide reports that commonly used rates of carbaryl could be expected to have a half-life in field soil of 38 days or less (3).

The National Soils Monitoring Program results for FY 1970 showed soil residues of carbaryl of about 1 ppm in 2.3% of the sites tested (43). Those states sampled that had carbaryl in soil were primarily in the southeast and the Great Lakes area.

A study by Caro, et al. (44) utilized an artificial watershed consisting of approximately two acres of a silt loam soil planted with corn. A collection system beneath the plot allowed measurement of runoff. The plot was treated with 4.5 lbs. per acre of carbaryl and 2 lbs. per acre of atrazine. The results of residue analysis of soil samples taken to a depth of 20 to 30 cm showed no significant loss of carbaryl in the first 40 days of the test. The overall value for the watershed for 95% dissipation of the carbaryl from the soil was 135 days. Previous investigation obtained a half-life of carbaryl in soil of 8 days which would result in 95% residue reduction in 35 days. There were localized differences in carbaryl dissipation in small areas throughout the watershed. In all areas there was a lag of 25 to 116 days before any dissipation of carbaryl from the soil. This lag period is indicative of microbial degradation. Once degradation began, it proceeded at a fairly rapid rate in all areas of the watershed.

3.3.2 Adsorption, Leaching and Runoff

This persistence of carbaryl in soil is influenced by soil type primarily because of the differences in the adsorptive characteristics of various soils. Carbaryl adsorbs readily to organic soils but moves rapidly through inorganic soils. Dissipation of carbaryl from field soils low in organic matter may not be due entirely to degradation but may be due in part to leaching.

Leenheer and Ahlrichs (17) studied adsorption of carbaryl on soil organic matter surfaces and found that adsorption was completely reversible. The amount of carbaryl that could be desorbed increased as the soil temperature increased from 5 to 40°C. The adsorption was thought to be due to weak chemical bonding between the hydrophobic portions of the pesticide molecule and soil particle.

The desorption of carbaryl with water was investigated by LaFleur (45) in soils with 5.16 and 0.15% organic matter. The K_b or ratio of the amount of carbaryl retained to the amount desorbed was 3.7 for the organic soil compared to 0.12 for the inorganic soil. These ratios indicate that organic soil adsorbs carbaryl more tightly than inorganic soil. Carbaryl residues were extracted from each soil at various depths of a soil column. Seventy-two percent of the carbaryl in the organic soil was found in the upper 20 cm; no carbaryl was found below 60 cm of the 100 cm column. The carbaryl was not very mobile in the organic soil. Only half of the carbaryl applied to the inorganic soil was retained in the column. This carbaryl was very mobile being evenly distributed throughout the column.

A few field studies on the leaching characteristics of carbaryl have been done. Klein, et al (32) performed lysimeter and field studies of land wastewater disposal sites. Carbaryl at 0.1 ppm was added to the wastewater effluents treated in the spray irrigation systems. No residues of carbaryl were detected in soil samples to a depth of 36 inches during the 14 week stabilization period for the disposal system and 26 weeks after addition of carbaryl to the wastewater. At this low concentration carbaryl is apparently degraded rapidly enough so that it doesn't translocate with the soil water and would not accumulate in spray irrigation systems.

In the watershed study by Caro, et al (44) the measurement of runoff after any rainfall indicated steadily decreasing amounts of carbaryl in runoff and accompanying sediment. The amount of carbaryl in runoff water and sediment was reduced substantially in three weeks and measured less than 0.1 ppb 70 days after application of carbaryl to the soil. Over 90% of the carbaryl detected in the runoff was found in a single sample taken after a heavy rainfall. Of the approximately 8.8 pounds of carbaryl applied to the plot, only 0.14% was recovered in runoff water and sediment. The soil in the watershed was a silt loam with 1.7% organic matter.

3.3.3 Microbial Degradation

Microbial degradation appears to be a major contributing factor to carbaryl dissipation in soils. Bacteria and fungi have been shown to decompose carbaryl primarily to CO_2 and 1-naphthol with several hydroxylated products and some as yet unidentified products also formed. The end products produced by fungi and bacteria are not identical indicating that degradation occurs by more than one pathway. Bacteria and fungi have also been shown to degrade 1-naphthol to some extent even though it is toxic to microorganisms. Chemical hydrolysis will also occur in alkaline soils.

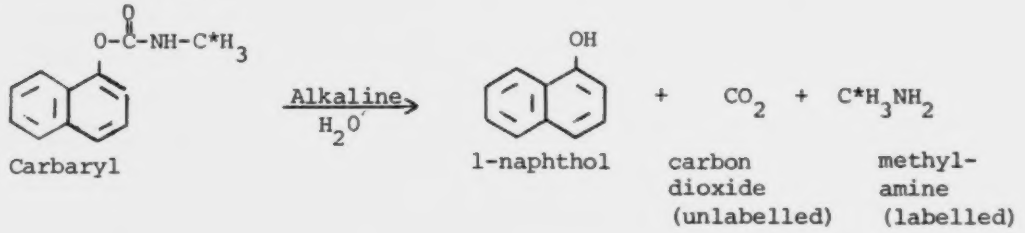
Microbial degradation was studied by Rodriguez and Dorough (46) in soils receiving varying degrees of carbaryl treatment. Soil A received no pesticide, soil B received a treatment of 4 lbs per acre of carbaryl six months previous to the experiments, and soil C had been treated with several pesticides, including carbaryl, over a period of 15 years. Carbaryl was added to the soils at 10 ppm. The most rapid decrease in carbaryl was observed in soil B between the first and second day after treatment. On the fourth day after treatment soils A and C retained over 90% of the carbaryl applied whereas soil B retained only 28%. At 120 days, however, 14 to 30% of the carbaryl was still present in all three soils. Recent application of carbaryl to soil appeared to facilitate the immediate decomposition of added carbaryl but had little effect on the long term rate. Autoclaved soils did show reduction in carbaryl over time but at a slower rate than in nonsterile soils. After 14 days incubation, autoclaved soil B retained 71% of added carbaryl as compared to 19% for nonsterile soil B. Also in autoclaved soil B there was no evolution of CO_2 or formation of 1-naphthol, which in other studies have been identified as microbial degradation products (47,48,49). Carbaryl in culture media with bacteria, fungi and nonsterile soil retained the following % of added carbaryl after 14 days incubation (46):

bacteria, 10 to 0% (one bacterium, 53%)
fungi, 54 to 79%
soil B, 19%
uninoculated control, 76%

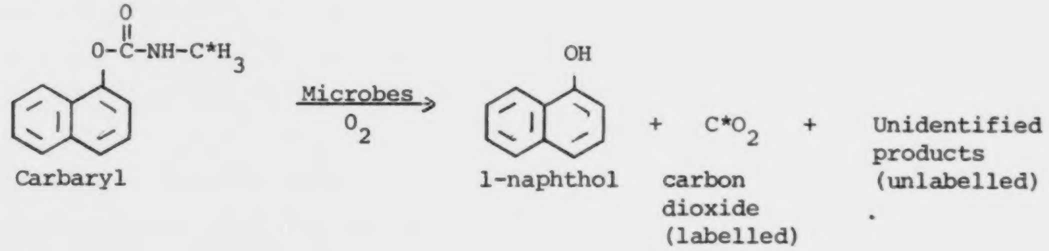
Dissipation of carbaryl in the uninoculated control was probably due to chemical hydrolysis.

Microbial degradation of carbaryl in soil was demonstrated by Bollag and Liu (49) in studies using a fungus and two bacterial strains. The carbaryl used was radioactively labelled at the terminal methyl group and loss of radioactivity was used as a measure of degradation. Metabolites were analyzed by thin layer chromatography; 1-naphthol and several unidentified compounds were found. CO_2 evolution was not measured directly. Chemical hydrolysis to 1-naphthol was not considered to be a possible avenue of degradation in these experiments because of the end products formed. The lost label was on the methyl carbon and not the carbonyl carbon that forms CO_2 in chemical hydrolysis. Uninoculated controls, in which chemical hydrolysis took place, showed no loss of radioactivity.

Chemical hydrolysis:


O-C-NH-C*H3
O
Carbaryl
Alkaline
H2O
OH
1-naphthol
+
CO2
+
C*H3NH2
carbon dioxide (unlabelled)
methyl-amine (labelled)

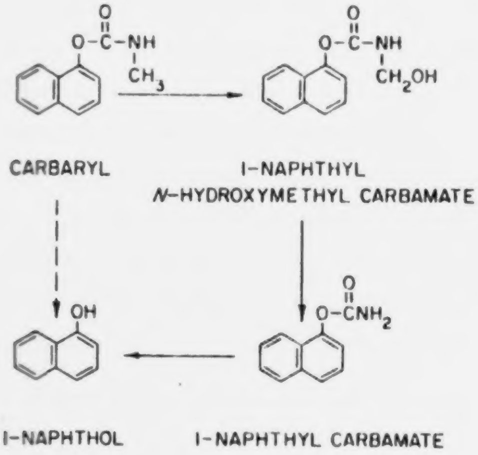
Microbial degradation:


O
O-C-NH-C*H3
Carbaryl
Microbes
O2
OH
1-naphthol
+
C*O2
+
Unidentified products (unlabelled)
carbon dioxide (labelled)

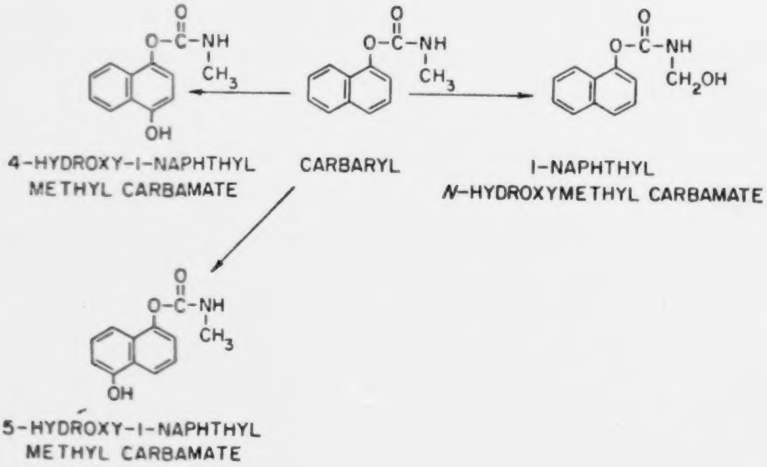
In comparison with the bacteria, the fungus, Fusarium solani, was a more effective decomposer of carbaryl, decreasing radioactivity by 24% in 5 days and 82% in 12 days (49). The two bacterial strains degraded 40 and 50% of the carbaryl in 12 days. Bacterial end products were not the same as those of the fungus. Mixed cultures of the three organisms were generally more effective than pure cultures, degrading from 65 to 80% of added carbaryl in 12 days.

The metabolism of 1-naphthol by these organisms was also studied in the same series of experiments. Even though 1-naphthol was toxic to the organisms in concentrations from 50 to 20 ppm, it was degraded to some extent by all three microbes. The fungus and the mixed cultures were the most active in decomposing 1-naphthol compared to pure cultures of the bacteria.

A mechanism of microbial degradation of carbaryl to 1-naphthol was proposed by Bollag and Liu (48):


CARBARYL
1-NAPHTHYL N-HYDROXYMETHYL CARBAMATE
1-NAPHTHOL
1-NAPHTHYL CARBAMATE

This study involved degradation of carbaryl by a fungus, Aspergillus terrus. The metabolism of carbaryl by another fungus, Gliocladium roseum, resulted in three hydroxylation breakdown products, two ring hydroxy and one methyl hydroxy compounds (48):

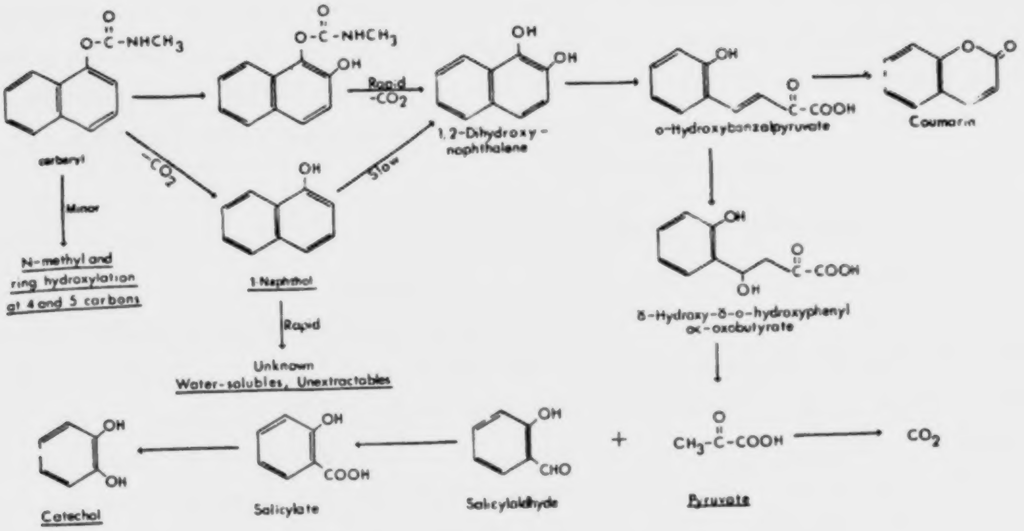

4-HYDROXY-1-NAPHTHYL METHYL CARBAMATE
CARBARYL
1-NAPHTHYL N-HYDROXYMETHYL CARBAMATE
5-HYDROXY-1-NAPHTHYL METHYL CARBAMATE

Kazano, et al (47) studied the degradation of carbaryl in five rice paddy soils with varying amounts of organic matter. Carbaryl radioactively labelled at the carbonyl carbon and the ring and labelled 1-naphthol were added separately to the soils at concentrations of 2 and 200 ppm. Degradation was measured as evolution of labelled CO_2. Degradation products were determined by thin layer chromatography. The CO_2 evolution measured ranged from 2.2 to 37.4% of the added carbaryl depending upon soil type and carbaryl concentration. The greatest amount of degradation occurred in the clay soil and the least in the loamy sand. Hydrolysis was the main pathway of degradation as determined by analysis of end products. In each soil there was some residual radioactivity left after solvent extraction. This nonextractable fraction appeared to be related to soil organic matter content; the soils with relatively high organic matter retained the higher percentage of the residual label. For example, a 13% organic soil retained 57% of the label in the unextractable fraction and soils with 1.5 and 4.1% organic matter retained 17%.

Evolution of CO_2 from 1-naphthol in soil was dependent upon soil type and 1-naphthol concentration (47). After 60 days incubation an average of about 6% of the radioactivity in the 1-naphthol evolved as CO_2, 11% was extracted with solvents and 78% remained in the soil as nonextractable residues (5% was lost in analysis).

A bacterium of the genus *Pseudomonas* was isolated from the rice paddy soils that metabolized 1-naphthol (47). 7.4% of the label evolved as CO_2, indicating cleavage of the naphthol ring. One of the metabolites identified was coumarin which is an artifact of a proposed pathway for naphthalene decomposition. The presence of coumarin indicates that the 1-naphthol pathway could be similar to that of naphthalene.

Based on the investigations by Kazano, et al (47) and others, Kuhr and Dorough (50) have proposed the following hypothetical pathway for microbial degradation of carbaryl in soil (products underlined have been identified as soil metabolites of carbaryl):


carbaryl
Minor
N-methyl and ring hydroxylation at 4 and 5 carbons
-CO2
Rapid
-CO2
1-Naphthol
Rapid
Unknown
Water-solubles, Unextractables
Slow
1,2-Dihydroxy-naphthalene
o-Hydroxybenzalpyruvate
Coumarin
δ-Hydroxy-δ-o-hydroxyphenyl α-oxobutyrate
Catechol
Salicylate
Salicylaldhyde
+
Pyruvate
CO2

3.4 FATE IN WATER

Carbaryl enters forest streams primarily by direct application as a consequence of forest spraying. The fate of carbaryl in water is determined by the effects of dilution, degradation, and adsorption to bottom sediments. Investigations of carbaryl in water are primarily laboratory studies of decomposition and measurement of residues.

3.4.1 Residues in Water

Residues of carbaryl were measured in spring and creek water following application of 1 lb per acre of Sevin-4-oil to forest test plots (12). An irregular pattern of carbaryl concentration was found in the water with residues ranging from 2 to 260 ppb 2 to 3 hours after application. The use of an oil formulation was thought to produce local accumulations of carbaryl in floating oil.

The persistence of carbaryl in water has been found to be dependent on pH and temperature (26). In a study by Szeto, et al (26) creek and pond water samples containing 1 ppm of carbaryl were incubated at 9°C with and without sediment. Autoclaved and non-autoclaved samples were also analyzed. Persistence of carbaryl in the creek water having a pH of 7.0 to 7.1 was greater than in the slightly alkaline pond water, pH 7.5 to 7.8. After 21 days incubation about 66 to 62% of added carbaryl remained in creek water whereas 46 to 39% was found in pond water. Autoclaving and the presence of sediment also increased persistence. In the pond water incubated with sediment there was a steady decrease in the carbaryl concentration of the water but the sediment concentration remained about the same from 2 days after inoculation through day 21 of the experiment.

3.4.2 Photodecomposition in Aquatic Systems

Statements regarding the stability of carbaryl in sunlight indicate conflicting views. Some researchers, including those of Union Carbide, report that carbaryl is stable in daylight including ultra violet light (2,11,36) Other investigators, however, report photodecomposition of carbaryl and its metabolites under various conditions (31,33,51). One study involved irradiation of carbaryl in ethanol (33). Several products were formed including 1-naphthol and methylisocyanate. Some of these products had anticholinesterase activity. One-naphthol was also a photoproduct in aqueous solution. Wauchope and Haque (31) state that acidic solutions of carbaryl and 1-naphthol are stable for weeks at room temperature under laboratory light. However, in basic solutions carbaryl and 1-naphthol decompose forming at least one light sensitive product. The carbaryl hydrolyzes in basic solution to 1-naphthol and 1-naphthol forms 1-naphthoxide ion. This ion appears to be light sensitive, reacting to give a quinone, lawsone.

Wolfe, et al (33,51) studied photolysis of carbaryl under various laboratory conditions. Sunlight was approximated by Pyrex-filtered light from a mercury lamp. Because chemical hydrolysis does not occur to any appreciable extent at pH values less than 7, the experiments were carried out in aqueous solutions of pH 5.5 to 6.9 in order to ensure that observed decomposition was due primarily to the action of the light. Their results indicate that photolysis of carbaryl in aquatic systems does occur in sunlight. However, 1-naphthol and methylisocyanate were not products of this photolysis system (33). The photolysis rate is slowed by the presence of oxygen and is not influenced by pH in acid solutions of pH 5 to 7. The calculated half-life for carbaryl at 30-40°N latitude of 45 to 46 hours agrees with a measured half-life in sunlight of 45 hours in distilled water buffered to pH 5.5. Table 5 lists the calculated half-lives in shallow water for carbaryl at various seasons and latitudes.

TABLE 5. CALCULATED DIRECT PHOTOLYSIS HALF-LIVES OF CARBARYL AT DIFFERENT SEASONS AND LATITUDES IN THE NORTHERN HEMISPHERE (33)

Latitude, °N	Half-life, hrs*			
	Spring	Summer	Fall	Winter
0	43	45	41	43
30	51	46	68	103
40	64	52	102	200
50	90	61	186	571
70	292	121	1760	43800

*Calculated for mid-season and for depths of 10 cm in pure water

Several factors determine the extent to which sunlight will influence the decomposition of carbaryl in forest streams. The level of dissolved oxygen, pH and the amount of incident radiation appear to be important. The variation of photolysis half-life with season, as determined by Wolfe, et al (51) indicates that at the time of application in the summer months photolysis rates can be as much as four times the rate in the winter months.

3.4.3 Chemical Degradation: Hydrolysis in Water

The rate of hydrolysis of carbaryl is rapid enough to be a significant degradation pathway likely to occur in nature (52). Hydrolysis rates are affected by temperature and pH (31). The following are half-lives of carbaryl in sea water of pH 8 at varying temperatures (31,34):

Temperature, °C	$t_{1/2}$
3.5	1 month
17	4.8 days
20	3.5 days
28	1.0 days

Carbaryl is stable at pH values from 3 to 6. Wolfe, et al (51) observed no decomposition of carbaryl in 10 days in water at 47°C and pH 5. Rapid hydrolysis of carbaryl to 1-naphthol, however, occurs at pH values above 7. The following are half-lives of carbaryl in water at varying pH levels (33):

pH	$t_{1/2}$
9	3.2 days
8	1.3 days
7	13 days
6	4.4 months
5	3.6 years

A study of the fate of carbaryl in estuarine water and mud was made by Karinen, et al (34). Carbaryl radioactively labelled at the carbonyl carbon and at the ring carbon was added at concentrations up to 25 ppm to sea water (pH 8) and sediment. Two systems were set up, one at 8°C and the other at 20°C. Dissipation of carbaryl and evolution of CO_2 was considered indicative of degradation.

At 8°C recoverable carbaryl residues in sea water containing sediments decreased with only a slight increase in the 1-naphthol concentration. A corresponding increase in carbaryl and 1-naphthol was found in the sediment. The carbaryl was adsorbed to the mud and slowly degraded. Sea water alone at 8°C did not degrade the added carbaryl to an appreciable extent; 90% was still present after 38 days. At 20°C carbaryl quickly dissipated to about 50% of the original concentration in 5 days and then slowly degraded. At 5 days the 1-naphthol formed began to decompose. CO_2 evolution from the carbonyl group began on the first day of the experiment; CO_2 from the ring structure began to appear on day 5. Inability to recover more than half of the label from the 20°C system lead to speculation that a non-reactive gas such as methane was also a product of degradation. Other investigations have observed the retention of label (e.g., unextractability with solvent) in soil and sediment (47,53). The results of this study show that carbaryl is likely to persist in estuarine mud from 2 to 6 weeks (34).

In a laboratory study Pritchard (53) investigated degradation of carbaryl in experimental ecosystem chambers containing sterile and nonsterile water and sediment from a salt marsh and from a toxic waste disposal pond. Varying amounts of unextractable material were found in all systems. This material may be polymers or cell biomass. Products of carbaryl degradation in nonsterile water were 1-naphthol and CO_2. No CO_2 was evolved and only 5.3% of added carbaryl was in the form of 1-naphthol in the sterile water. Several other unidentified products were formed in both systems.

4.0 IMPACTS ON NON-TARGET ORGANISMS

Forestry use of carbaryl can be expected in general to affect insect and arthropod populations and the aquatic biota in the area being sprayed. Carbaryl exhibits little phytotoxicity and its effect on wildlife, including birds, appears to be minimal. The high toxicity of carbaryl to honey bees is probably the major hazard to non-target organisms in forest applications. Some fish and certain aquatic invertebrates, including insects, have also been shown to be particularly sensitive to carbaryl. Table 6 lists carbaryl toxicities to various organisms.

Natural waterways in forested areas are the ecosystems most vulnerable to injury by carbaryl contamination. Protection of sensitive arthropods that are food for fish is of critical importance in maintaining balance in the system (54). Chronic exposure of aquatic biota is unlikely because carbaryl is usually applied to forests only once a year. Newton and Norgren (54) propose that maintenance of 0.2 ppb in large rivers with somewhat higher concentrations in feeder streams should provide adequate protection against short term damage to aquatic systems due to a single forest application of carbaryl.

4.1 PLANTS

Carbaryl has very little phytotoxic effect. As noted in Section 1.1, carbaryl is used directly on a variety of crops for insect control. Under certain conditions, however, carbaryl can cause injury to some plants. For example, carbaryl has been reported to cause damage to Boston ivy, watermelons, apple leaves, apples and pears (2). The manufacturer warns users that some foliage may be injured if rain or high humidity persist for several days after application. Carbaryl causes young fruit to fall from apple trees if applied 10 to 25 days after full bloom and is used for fruit thinning (1).

4.2 FISH AND OTHER AQUATIC ORGANISMS

Carbaryl is toxic to fish with 96-hour median tolerance limits (LC_{50}) ranging from about 1 to 20 ppm (54). Fish are generally more sensitive to 1-naphthol than to carbaryl. One-naphthol at 1.3 ppm is reported to be twice as toxic to fish as carbaryl (57). Fingerling brown trout are less sensitive to carbaryl in soft, acidic water than in hard, alkaline water that fosters hydrolysis to 1-naphthol (57). The toxicity of carbaryl to fish increases as the water temperature increases. Carbaryl exhibits a corresponding increase in decomposition by hydrolysis with increasing temperature and sunlight (57). The formulation used may also intensify toxicity. For example, the 48-hour LC_{50} for goldfish is 28 ppm for Sevin-4-oil and 14 ppm for Sevin 50 WP (57).

TABLE 6. TOXIC DOSES OF CARBARYL FOR VARIOUS ORGANISMS (54,55,56,57,58)

Organism	Parameter	Toxic Dose*
1. Fish		
fathead minnow	TL_m, 96 hr	9.0 ppm
channel catfish	LC_{50}, 96 hr	15.8 ppm
brown trout	LC_{50}, 96 hr	1.95 ppm
Coho salmon	LC_{50}, 96 hr	0.764 ppm
goldfish	LC_{50}, 96 hr	13.2ppm (58)
	LC_{50}, 48 hr., Sevin-4-oil	28 ppm (59)
	LC_{50}, 48 hr., Sevin 50 WP	14 ppm (59)
2. Aquatic invertebrates		
crayfish	LC_{50}, 96 hr.	0.0086 ppm (54)
	TL_m, 96 hr.	2.43 ppm (55)
Dungeness crab	LC_{50}, 96 hr.	0.180 ppm
oyster	LC_{50}, 96 hr.	2.2 ppm
bay mussel	LC_{50}, 96 hr.	3.0 ppm
adult mactrid clam	TL_m, 96 hr.	125 ppm
grass shrimp	TL_m, 96 hr.	0.12 ppm
mosquitofish	TL_m, 96 hr.	31.8 ppm
3. Mammals		
rat	LD_{50}, oral, female	500 mg/kg (10)
	LD_{50}, oral, male	850 mg/kg (10)
	LD_{50}, oral	540 mg/kg (58)
rabbit	LD_{50}, 24 hr.	710 mg/kg
mule deer	LD_{50}, oral	200-400 mg/kg
4. Birds		
mallard duck	LD_{50}	2179 mg/kg
pheasant	LD_{50}	2000 mg/kg
	LC_{50}, oral	5000 mg/kg
Canada geese	LD_{50}	1790 mg/kg
sharptailed grouse	LD_{50}	780-1700 mg/kg
5. Insects		
stonefly	LC_{50}, 24 hr.	0.005 ppm
Daphnia	LC_{50}, 48 hr.	0.0064 ppm
gypsy moth	LD_{50}	0.26 μgm/moth
honeybee	LD_{50}	1.3 μgm/bee

* References are given for reports of different toxicities to the same organism.

Carbaryl can also have indirect effects on fish. Non-lethal concentrations of carbaryl have been shown to increase toxicity to trout of other pesticides, such as 2,4-D and dieldrin(24). Residues of less than 1 ppm in streams have resulted in the presence of drifting dead insects which could result in a change in the eating habits of the fish in these streams (24).

Depressed acetylcholinesterase levels of about 10 to 35% were detected in fish up to 8 days following forest spraying of 1 lb per acre carbaryl in Maine against the spruce budworm(24). No residues were found in fish tissue. Some dead fish were found in shallow waters after forest application of 0.75 lb per acre (24).

Korn (60) exposed channel catfish to carbaryl at 0.28 and 2.8 mg per kg per week in feed and to 0.05 and 0.25 mg/l in continuously circulating tank water for up to 56 days. Fish were sampled at intervals to determine residues of carbaryl and metabolites. Analysis of carbaryl residues in the fish indicated that carbaryl was metabolized and excreted by the fish and did not accumulate to any appreciable extent. Less than 1% of the available carbaryl was retained by fish exposed via diet. Only 0.0001% of carbaryl was retained by fish exposed via water. Diet exposed fish placed on carbaryl-free diets rapidly eliminated the carbaryl. Water-exposed fish placed in carbaryl-free water maintained previous residue levels.

Carlson (56) investigated the effects of long and short-term exposure to carbaryl on the growth, survival and reproduction of the fathead minnow. Carbaryl in tank water for 6 to 9 months at about 0.7 ppm adversely affected survival, egg release, spawning and egg development. Short-term exposure indicated a 96-hour TL_{50} of 9.0 ppm.

Toxicity of carbaryl to aquatic organisms other than fish has been studied by a number of investigators. Forest use of carbaryl has been reported to reduce populations of aquatic invertebrates in streams and ponds (36). The toxicity of carbaryl to crustaceans and mollusks is greater than its toxicity to fish. Most reported 96-hour LC_{50}'s range from about 10 ppb to 3 ppm. Some mollusks are especially sensitive to carbaryl; development of clam eggs is inhibited by 1 ppb (57,58).

Tagatz et al (61) investigated the effects of low concentrations of carbaryl on the numbers of individuals and species in estuarine communities that developed from planktonic larvae in contaminated tanks. One-naphthol concentrations were not measured. Since sea water is alkaline, hydrolysis of the carbaryl to 1-naphthol could have occurred in the experimental tanks. Carbaryl (or 1-naphthol) concentrations of approximately 10 and 100 ppb added to the tank water after 10 weeks resulted in a decrease of about 50% in the number of species and a significantly smaller number of species per tank. At 100 ppb there was a complete absence of nemertan worms and a two-fold increase in one species of annelid worm. This study demonstrated a distinct effect of 0.1 ppm carbaryl (or 1-naphthol) on the natural composition of an estuarine community.

Chaiyarach et al (55) determined carbaryl median tolerance limits for freshwater and marine animals important in the food webs in areas around Texas rice fields routinely sprayed with carbaryl. The freshwater animals tested were mosquitofish, grass shrimp and crayfish; the marine animal tested was the mactrid clam. Sevin 80WP was used and added both as a powder and in an acetone solution. The powder was found to be slightly more toxic than the liquid probably because of its ability to coat the gills and prevent gas exchange. The results of the bioassays with carbaryl powder are presented in Table 7. As shown in Table 7, the clam was the most tolerant of the species tested perhaps because it can close its shell and avoid prolonged exposure to the pesticide (55). The 24-hour TL_m for grass shrimp was found to be 0.41 mg/l for carbaryl powder and 0.42 mg/l for carbaryl in acetone. A previous study reported values of 0.042 mg/l for the 24 hour TL_m. The difference was thought to be due perhaps to the development of an increased resistant species in this geographical location.

TABLE 7. TL_m, mg/l FOR CARBARYL POWDER (55)

Organism	24 hr.	48 hr.	72 hr.	96 hr.
mosquitofish	40	35	32.4	31.8
grass shrimp	0.41	0.24	0.14	0.12
crayfish	2.87	2.66	2.43	2.43
mactrid clam	>2000	1860	350	125

A three-year study was done in New York state on the effects of forest spraying of 1 lb per acre of carbaryl on the aquatic environment (59). This study found no adverse effects on the watershed monitored due to carbaryl. Residues greater than 0.1 ppm were not detected in water, soil or insects. No change in the aquatic insect population could be attributed to the spraying.

4.3 WILDLIFE

Few studies have been done on the effects of carbaryl on forest animals. The toxicity of carbaryl to mammals and birds, however, appears to be less than that to aquatic organisms. Carbaryl is used on cattle, poultry, and pets to control insects. Reported LD_{50}'s for mammals range between 200 and 850 mg/kg indicating moderate toxicity. LD_{50}'s for birds are reported to range from 780 to 2300 mg/kg indicating only slight toxicity. Mammalian carbaryl toxicity studies discuss effects on the survival and reproduction of small mammals whereas bird studies emphasize measurement of brain cholinesterase levels and observation of physical effects.

Barrett (62) investigated effects on cotton rats, house mice and old-field mice feeding in a millet field sprayed with 2 lb per acre of carbaryl. The millet contained about 35 ppm carbaryl resulting in a consumption of about 1.1 mg carbaryl per adult per day. The carbaryl in the diet produced a four week delay in reproduction of the cotton rat. The lag in the population density growth rate allowed another species to become dominant. There were no observed effects on the old-field mouse population. The house mouse population increased somewhat due to the temporary decrease in cotton rats.

Subsequent laboratory studies on reproduction in the cotton rat and house mouse gave results similar to the field study (62). The number of litters born and the number of females giving birth were reduced by more than 50% in cotton rats fed 1.1 mg per day of carbaryl. Reproduction in the house mouse was not affected.

A Russian study of a forest application of 4.46 lb per acre (0.5 gm per m^2) of carbaryl noted decreases in mole and rodent populations without observable recovery in two years (38). Residues of carbaryl were detected in moles. Reproductive organs contained 5 mg/kg, liver contained 3 mg/kg and muscle tissue contained 1.5 mg/kg. Another study of application of 0.5 lb per acre to grassland reported observation of several dead deer mice in the treated area (5). A Canadian study found no change in small mammal populations two months after forest spraying of Sevin-4-oil against the spruce budworm (63).

The reported effects of carbaryl on birds include temporary territory abandonment (7), loss of food supply (64), decreased growth (65), increased relative liver and kidney weights (65), and depressed brain cholinesterase activity (28,29). Kurtz and Studholme (66) measured residues of carbaryl in ground feeding songbirds inhabiting an area sprayed with 1 lb per acre of carbaryl. Three days after spraying, trace (0.1 to 1.0 ppm) amounts were found in both exposed and unexposed birds. In this study ground-feeding birds were tested as opposed to canopy-feeding birds. If the amount of carbaryl spray reaching the ground was small, it could account for the lack of recoverable residues in the birds. Carbaryl ingested could also have been rapidly metabolized and excreted. Bart (64) surveyed several forest plots before and after carbaryl application of 1 and 5 lb per acre. Observations were made for the presence or absence of birds and song frequency. No effects due to spraying were detected. Numbers of birds remained the same; none left the area to forage. Nesting, song frequency and weight gain were normal. Buckner, et al. (63) reported no change in songbird population up to 3 weeks following carbaryl spraying of a Canadian spruce forest against the spruce budworm.

Cholinesterase inhibition has been used as a measure of the magnitude and extent of exposure of forest birds to carbaryl. Zinkl, et al. (28) determined brain cholinesterase levels in 12 species of birds up to 5 days after forest application of 1 lb per acre of Sevin-4-oil. Three birds of different species showed depressed values. One bird, collected the day of spraying, had enzyme levels greater than 20% below the mean of the control group. Only 3.4% of the birds exhibited enzyme inhibition indicating that exposure was minimal. The authors proposed that sublethal cholinesterase inhibition could increase susceptibility to predation and impair ability to obtain food (28).

Richmond et al (29) measured brain cholinesterase levels as well as several other parameters in forest birds to determine the effects of a carbaryl forest treatment at 2 lb per acre (an application rate which would normally be used against the Douglas-fir tussock moth). Measurements were made of breeding bird density, species diversity, nesting success (survival of eggs or nestlings), brain cholinesterase, abnormal behavior, and presence of sick or dead birds. Two of the 55 birds tested showed enzyme levels depressed by 23 and 27%. All other measurements were normal. No abnormal behavior, sick or dead birds were observed. Since at the time of spraying there was no insect outbreak, this study did not measure the effects of carbaryl on birds due to ingestion of contaminated insects. In another field investigation where carbaryl was used to control an actual outbreak of gypsy moth, a 55% decrease in bird population was noted (29).

Laboratory studies of quail exposed to large doses of carbaryl in daily feed have shown effects on growth and organ weight (65). Increased length of exposure intensified observed effects. The presence of carbaryl in parental diet did not effect offspring. Levels in feed of 900 mg/kg of body weight or less for 14 weeks resulted in decreased body weight and increased brain, liver and kidney weight. Liver and kidney weight gain and morphological change were thought to be related to detoxification. The progeny of exposed quail exhibited normal growth, reproduction and mortality rates. Another experiment with chick embryos involved exposure to mixtures of pesticides by injection into the egg (67). Only 40% of eggs injected with 5 mg of carbaryl hatched. Only 4% hatched of those eggs injected with 2.5 mg each of phosdrin and carbaryl. No eggs hatched that were injected with 2.5 mg each of malathion and carbaryl. Doses for these chick embryos were massive in terms of expected environmental exposure.

4.4 BENEFICIAL INSECTS

Carbaryl is a fairly broad spectrum insecticide and so affects many beneficial insects as well as target insects. Honey bees are particularly susceptible to the toxic effects of carbaryl. The LD_{50} in μg a.i. per bee is 1.3 (2). Certain soil insects and various aquatic insects are also very sensitive to carbaryl. Its lethal effect on aquatic insects serves to decrease the supply of fish food in streams and ponds.

Croft and Brown (68) report an LD_{50} for the gypsy moth of 0.26 μg carbaryl per insect. Corresponding LD_{50}'s for parasites of the gypsy moth range from 1.0 to 0.03 μg per insect. Coster and Ragenovich (69) investigated the effects of carbaryl on 11 species of predators and parasites of the southern pine beetle. Infested pine trees were cut down and sectioned into four foot bolts. The center bolts were sprayed with 2.2% carbaryl and caged. Those insects that emerged from the treated bolts were counted and compared to emergence from untreated bolts. Five of the 11 species counted showed significant decreases in emergence from treated bolts. Numbers of the most common beneficial insect were decreased to 1/3 of the control.

Spain (70) studied the litter fauna of plots of a Corsican pine forest sprayed with approximately 10 and 1 lb per acre of carbaryl. Litter samples for invertebrates, especially insects and mites, were taken at 11 days and 3-1/2, 7 and 10-1/2 months. Statistical analyses indicated that the lower dose of 1 lb per acre caused no decrease or only a slight decrease in most invertebrate populations. Collembola, springtails, showed a marked decrease in numbers even at the lower dose. Mite populations were generally unaffected. Populations of other invertebrate groups surveyed were significantly different from the control when exposed to 10 lb per acre of carbaryl (10 times the normal application rate). These population numbers had not returned to normal by 10-1/2 months. Once the carbaryl in the soil is degraded, the invertebrate populations should return to normal but the composition of the litter will have changed. New populations will develop from surviving and immigrant invertebrates.

Barrett (62) investigated the effects on arthropods of 2 lb per acre of carbaryl applied to a millet field. Arthropods were sampled before and after spraying; density, biomass and species diversity of 1° and 2° consumers were determined. All three parameters for 1° and 2° consumers were decreased after treatment. Total biomass and numbers of insects were reduced over 95%. Phytophagous insects (1° consumers) were generally more susceptible to carbaryl than predators (2° consumers) and returned to normal in 2 weeks as opposed to 5 weeks for predators. In a similar study, Suttman and Barrett (71) compared the response to 2 lb per acre of carbaryl to an old, undisturbed field and a newly-planted oat field monoculture. Arthropod density, biomass and species diversity were measured before and after treatment. The effects of carbaryl on arthropods for herbivores (1° consumers) was immediate, pronounced and short term, whereas for carnivores (2° consumers) it was delayed, less pronounced and long-term. Decreases in arthropod density and biomass were greater and recovery was more rapid in the old field indicating that the more stable, diverse ecosystem was more resilient than the monoculture.

Pre- and post-spray populations of insects were compared by Dean, et al. (72) in New York forests aerially treated with 1 lb per acre of carbaryl against the gypsy moth. Predator populations were represented by the Calosoma beetle; soil forming decomposers were represented by mites and Collembola, springtails. Measurements of the amount of carbaryl actually reaching the ground indicated large variations with an average of 0.145 lbs per acre to the soil. The Calosoma beetle and Collembola populations were depressed following treatment and for 3 months afterward but returned to normal the following spring. A significant (30%) increase in mites occurred probably due to decreases in predator and/or competitor insect populations. This increase was temporary; the mite population was also back to normal the following spring.

The effect of carbaryl on aquatic insects has also been investigated. The application of 1 lb per acre of carbaryl to a watershed resulted in stream residues of 40 to 80 ppb carbaryl (24). This concentration produced drifts of dead stoneflies, mayflies and caddisflies in the stream. In similar studies the population of aquatic insects was reduced 60 to 100% (24). Long term effects have also been reported. Some populations of aquatic insects did not return to normal up to 2 years after exposure (24).

Carbaryl is highly toxic to honeybees producing high bee mortality in sprayed areas (24). Bee poisoning is indicated by agitated behavior, death of many bees and queenless hives (73). A queenless hive or one severly damaged will not live through the following winter. Severe poisoning in one instance left one-half of the colonies of a sprayed area without queens within 30 days of exposure (73). Carbaryl applied as a wettable powder can be collected by the bee along with the pollen and transported back to the hive (24,73). The carbaryl in the hive can be incorporated into the pollen stores and fed to newly emerging bees. Thus, carbaryl can be toxic in the hive for up to 8 months. The oil formulation is not as easily collected by bees and its use is thought to reduce the hazard of carbaryl to bees (20,22,23,24).

The Sevin label contains a warning that spraying will harm bees in the spray area. To avoid bee poisoning, hives should be moved beyond bee flight range (3 to 4 miles) until one week after carbaryl application (2,73). Carbaryl should not be applied at a time when bees are foraging or when ambient temperatures are unusually low. At low temperatures residues on crops remain toxic to bees up to 20 times as long (73).

A series of investigations were carried out in the forests of northeastern Oregon to determine the effects of carbaryl spraying against the Douglas-fir tussock moth. Application of Sevin-4-oil at 2 lbs per acre left residues on foliage of 39 to 145 ppm on the day of spray (20). Residues of 14 ppm were found in bee pollen one day after spray. Nearly 50% bee mortality was observed during the first week (22). Three of the 4 hives in the area were dead by the following January. The following spring, however, the number of foraging bees returned to normal due to migration of bees into the area. There was no decrease the following year in fruit production of wild plants due to lack of pollination. Predator ant and yellowjacket populations also showed no long term effects due to the one carbaryl application (23).

4.5 MICROORGANISMS

Carbaryl toxicity has been noted for marine and freshwater algae and for soil microbes. Carbaryl at 1.0 ppm suppressed growth of two species of marine algae; 10 ppm was lethal for three species (61). Five species of phytoplankton could not tolerate concentrations of carbaryl greater than 0.1 ppm (61).

The effect of carbaryl on freshwater algae varies with the algal genus (35). Carbaryl at 0.1 ppm is toxic to Chlorella but Scenedesmus appears to thrive on it. When exposed to carbaryl, Scenedesmus cell biomass increased by 44 to 57% in 6 days (35). Breakdown of carbaryl to CO_2 and NH_3 provides nitrogen to aquatic ecosystems; if nitrogen is a limiting nutrient, carbaryl in natural waters could produce algal blooms.

Barrett (62) in his study of the millet field sprayed with 2 lbs per acre of carbaryl found a significant decrease in litter decomposition 3 weeks following treatment. The decrease was attributed to the change in the microarthropod population.

The carbaryl hydrolysis product, 1-naphthol, is toxic to microorganisms. Bollag and Lui (47) in their investigation of carbaryl and 1-naphthol degradation by soil microorganisms determined that Fusarium solani can tolerate up to 50 ppm and certain bacteria 20 to 30 ppm of 1-naphthol.

4.6 BIOACCUMULATION

Bioaccumulation has been studied in various organisms but has been observed primarily in aquatic biota. Carbaryl has been shown to accumulate in trout bile (30). The ratio of carbaryl and metabolites in bile to carbaryl in aquarium water was measured as 1064. The ratios of fish tissue concentration to water concentration are not as high. An aquarium concentration of 2.6 ppm resulted in ratios for lake trout of 3.6 and for Coho salmon of 4.0 (30). Storage factors in animals are reported as the ratio of carbaryl in tissue to carbaryl in the diet. Animals tested show low ratios; the ratio for the cow kidney is 0.01 and for the chicken kidney is 0.006 (30).

Kanazawa et al (21) investigated the fate of carbaryl in an experimental aquatic ecosystem. Carbaryl concentrations were monitored in soil (bottom mud), water and tissues of various aquatic organisms. The soil or mud was the major repository for carbaryl in this ecosystem. After 20 days about 68% of the radioactivity added as labelled carbaryl was found in the soil, 45% as unextractable residues. The unextractable residues were non-toxic to Daphnia which is very sensitive to carbaryl. The water in the system contained about 1% and biomass about 0.1% of the added carbary label. Bioaccumulation ratios (BAR's) were calculated as ppm carbaryl in dry tissue to ppm carbaryl in the final test water. The results were as follows:

Source	ppm Carbaryl	BAR
Soil	1.55	
Water	0.00945	
Algae	37.9	4000
Duckweed	34.2	3600
Snail	2.81	300
Catfish	1.33	140
Crayfish	2.48	260

The ratios for algae and duckweed are relatively high. These results indicate that carbaryl can persist and accumulate in the aquatic environment. Biomagnification effects on food chains due to large accumulations of carbaryl in organisms of the first trophic level is not known.

5.0 MISCELLANEOUS

A number of issues have been raised regarding the real and potential consequences of carbaryl use in forestry. These topics include the toxicity and persistence of 1-naphthol, viral enchancement by carbaryl, possible formation of nitrosamines from carbaryl in soil and the large aerial carbaryl spray programs. These issues are briefly discussed in this section.

The main product of carbaryl decomposition is 1-naphthol. It is readily formed in an alkaline environment. There is some evidence that 1-naphthol is more toxic to fish and certain aquatic organisms than carbaryl itself (59). 1-naphthol is considered toxic by ingestion and skin absorption (41). Methods of determining carbaryl residues do not always differentiate between carbaryl and 1-naphthol (34,44) so that properties attributed to carbaryl may be due to 1-naphthol formed by hydrolysis prior to analysis.

The apparent microbial breakdown of carbaryl in soil to 1-naphthol could result in a more persistent compound than the original pesticide. Sjoblad et al (74) have isolated an extracellular fungal enzyme that catalyzes the polymerization of 1-naphthol to dimeric, trimeric, tetrameric and pentameric forms. Polymerization of 1-naphthol and its interaction with naturally occurring compounds could produce substances very resistent to microbial breakdown (47).

The gypsy moth has been a forest pest in the northeastern United States since 1869 (7). In these forests one to three years of a high population of gypsy moths is usually followed by seven years of low population due to the activity of natural enemies such as wasps, birds, mice, parasites and wilt disease virus. The use of a non-selective insecticide such as carbaryl can decrease populations of natural insect enemies as well as the gypsy moth. The main reason for massive spraying against such defoliating insects is to preserve the eocnomic value of the forest land. Commercial timber in Massachusetts, Rhode Island and Connecticut is minimal so that, in these states, the value of forested land is primarily in terms of recreational use (75). There is much controversy, especially in New England, over the effectiveness and desirability of large carbaryl spray programs. Some residents believe if no spraying is done, the gypsy moth's natural enemies will control the pest population as well as carbaryl but without the human and environmental exposure to pesticide (75). Some of the local objections to the large scale spray program against the spruce budworm are similar to the arguments against use of carbaryl for control of the gypsy moth. Some residents question the overall efficiency of carbaryl in actually controlling insect infestations in light of the hazards involved in its use (6).

Abrahamsen and Jerkofsky (76) have recently reported a 2 to 15 fold increase in virus production in cell cultures exposed to carbaryl. Although human virus and human cell cultures were used in these experiments, the same phenomenon may be exhibited by animal and plant viruses. Enhancement of viral disease in non-target organisms would be difficult to determine; viral disease is not monitored other than in domestic animals and birds.

Nitrosamines are known carcinogens in laboratory animals and have been found in certain pesticide formulations, excluding carbaryl (77). Carbaryl has been nitrosated; i.e., converted to a nitroso derivative, in the laboratory. However, no N-nitrosocarbamates were detected when three soils were tested with 100 and 1000 ppm nitrite and 20 ppm carbaryl (77).

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Common Name: Trichlorfon

Chemical Name: 0,0-Dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate

Trade Name: Dylox 1.5 Oil, Dylox 4

Major Applications in Forestry: Control of gypsy moth and spruce budworm

SUMMARY

Trichlorfon is an organophosphorus insecticide and parasiticide used in forestry primarily for the control of gypsy moth and spruce budworm. Trichlorfon kills insect pests by contact or through stomach action upon ingestion. Trichlorfon has only been recently used in forestry and, therefore, there is limited data regarding its environmental fate and potential ecological effects in forest applications.

DDVP or 0,0-dimethyl-0-(2,2-dichlorovinyl) phosphate is the only known metabolite of trichlorfon. DDVP (dichlorvos) is itself a registered insecticide and is considerably more toxic than trichlorfon. It is still not certain whether metabolism in plants involves production of DDVP. However, available data indicates that residues will degrade rapidly in new leaves and twigs, but can persist longer in forest litter.

Trichlorfon fate in soil is affected by adsorption, leaching, runoff and chemical and microbial degradation processes. Half life in soil is generally less than 30 days with most reported values below 6 days. Trichlorfon is subject to leaching and washout from soil due to its high water solubility. It breaks down in natural water relatively quickly, particularly under alkaline pH conditions and at warmer temperatures.

Laboratory studies indicate that trichlorfon is highly toxic to some aquatic invertebrates. Field studies have shown, however, that when trichlorfon is applied at recommended application rates, little adverse effects on fish can be expected. No impact on populations of soil microorganisms has been reported. Trichlorfon can reduce populations of some non-target insects; however, available data indicates trichlorfon is relatively nontoxic to honey bees. Trichlorfon has been shown to cause subacute effects in birds and in the white-footed mouse, as evidenced by depressed brain cholinesterase activity. There are reports that trichlorfon may be teratogenic in mammals.

1.0 INTRODUCTION

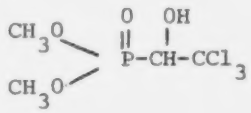
Trichlorfon is an organophosphorus insecticide and parasiticide originally developed by Farbenfabriken Bayer GmbH, Leverkusen, West Germany (1). In the United States, trichlorfon is formulated into finished products and marketed by the Agricultural Chemicals Division of Mobay Chemical Corporation under the trade name Dylox.

The trichlorfon formulation most commonly used in forest pest control is formulated in a refined petroleum oil and has the trade name Dylox 1.5 oil. Dylox 1.5 oil is registered and used for gypsy moth control at a dose of 1 lb a.i./acre (5.3 pints of formulation) (2). It contains 18.5 percent active ingredient , 76.2 percent refined petroleum distillates, and 5.3 percent inert ingredients (2). Dylox 4 is registered and recommended for use on the gypsy moth, spruce budworm (in Maine and New Hampshire), and forest tent caterpillars (in Louisiana and Alabama only) (3). It is mixed with water for application at 1 to 2 pints/acre and contains 39 percent active ingredient and 61 percent inert ingredients. In the 1979 spruce budworm suppression program in Maine, approximately 97,000 acres of forestland were treated with Dylox (4); no Dylox was used in the 1980 program.

Trichlorfon kills insects on contact or by stomach action upon ingestion by insects. It is registered for use on a wide variety of field crops, vegetables, seed crops, and ornamentals, and is effective for the control of many species of Diptera, Lepidoptera, Hymenoptera, Hemiptera, and Coleoptera (1).

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF ACTIVE INGREDIENT

The active ingredient of Dylox is 0,0-dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate:

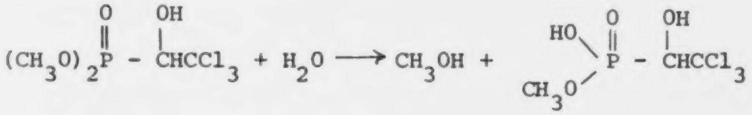


It is a white crystalline powder (determination of molecular weight shows that it is a bimolecular compound with intermolecular hydrogen bonds) (6) with a melting point of 81-82°C and a boiling point of 100°C at 0.1 mm Hg (18). Its solubility is as follows (7):

- 12.3 g/100 g in water.
- 15.2 g/100 g in benzene.
- 75 g/100 g in chloroform.

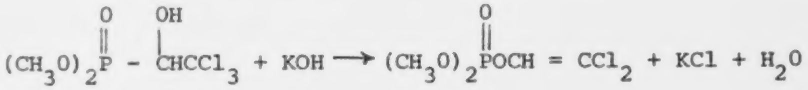
It is only slightly soluble in paraffinic hydrocarbons. The vapor pressure and volatility of trichlorfon are 7.8 x 10^{-6} mm Hg and 0.11 mg/m^3, respectively, at 20°C (6).

Trichlorfon is stable in acid medium and is rapidly hydrolyzed in alkaline medium. The hydrolysis under different conditions follows two paths. Under acidic conditions the first product of hydrolysis is 0-methyl-(1-hydroxy-2,2,2-trichloroethyl) phosphoric acid, which is further hydrolyzed with mineralization of the molecule (6):



$$(CH_3O)_2\overset{\overset{O}{\|}}{P} - \overset{\overset{OH}{|}}{C}HCCl_3 + H_2O \longrightarrow CH_3OH + \overset{HO}{\underset{CH_3O}{}}\!\!>\overset{\overset{O}{\|}}{P} - \overset{\overset{OH}{|}}{C}HCCl_3$$

Trichlorfon breaks down very rapidly in the light in dilute solutions. In alkaline medium trichlorfon is dehydrochlorinated and simultaneously rearranged. The principal product of the reaction is 0,0-dimethyl 0-(2,2-dichlorovinyl) phosphate (dichlorvos, DDVP) (6):



$$(CH_3O)_2\overset{\overset{O}{\|}}{P} - \overset{\overset{OH}{|}}{C}HCCl_3 + KOH \longrightarrow (CH_3O)_2\overset{\overset{O}{\|}}{P}OCH = CCl_2 + KCl + H_2O$$

Dichloroacetaldehyde, dimethylphosphoric acid, and some other compounds are formed as products of side reactions.

Prolonged storage of aqueous solutions of trichlorfon leads to partial hydrolysis of the compound which results in acidification of solutions, including formation of phosphoric and dimethylphosphoric acids, and HCl.

3.0 ENVIRONMENTAL FATE

3.1 UPTAKE AND METABOLISM BY PLANTS

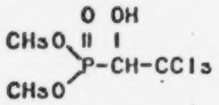
Limited data is available regarding uptake and metabolism in plants. Young cotton plants treated with ^{32}P-trichlorfon by root uptake and leaf application for periods up to 9 days were found to contain small amounts of trichlorfon (7). After 3 days, about 70 percent of the activity was accounted for as water soluble degradation products. Of this, 60-70 percent was dimethyl phosphate, 17-24 percent was inorganic phosphate, and less than 5 percent was monomethyl phosphate. In another study with ^{32}P-trichlorfon applied to individual cotton leaves, dimethyl phosphate was also found as a major metabolite (7). Minor amounts of O-dimethyl trichlorfon, DDVP, and O-dimethyl DDVP were reported. Figure 1 illustrates these possible plant metabolites of trichlorfon and dichlorvos.

Of all the compounds shown in Figure 1, only trichlorfon (parent compound) and its metabolite DDVP are biologically active and, therefore, of toxicologic significance (7). It should be noted that DDVP is a considerably more toxic substance than the trichlorfon. The acute oral LD_{50} of DDVP in the rat is 56-80 mg/kg whereas the LD_{50} for the Dylox formulation is 450-630 mg/kg (5).

3.2 PERSISTENCE ON FOLIAR SURFACES

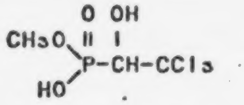
Available data indicates that neither trichlorfon or DDVP presents a residue problem (5,7). In a 1971 USDA study (8), trichlorfon residues on Douglas-fir, willow, and grass were monitored at several locations in the Pike National Forest in Colorado following an aerial application of 1 lb/acre. The results, presented in Tables 1 and 2 for two test plots, indicated a fairly rapid decline on foliage during the first two weeks after application. In general, residues taken from grass and willow growing in exposed areas showed a greater deposit; however, greater exposure also seemed to be correlated with a faster disappearance of the insecticide. Although the exact mechanism(s) for the dissipation of trichlorfon on foliar surfaces is not known, much dissipation is probably due to a combination of chemical degradation and photodecomposition.

Another study performed by the State University College of Forestry at Syracuse University (9) sought to determine the persistence of trichlorfon residues in the forest environment via a sampling and analysis of forest leaves, twigs and litter. Dylox 80% SPA formulation mixed with Sunspray 7N summeroil was aerially applied to a forest in New York at the rate of 1 lb/acre. At the two plots sampled, residue levels on leaves decreased from



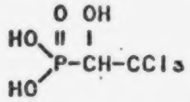
O,O-dimethyl-(1-hydroxy-2,2,2-trichloroethyl)-phosphonate

Parent Compound



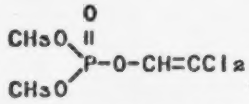
O-Methyl-(1-hydroxy-2,2,2-trichloroethyl)-hydrogen phosphonate

Des methyl trichlorfon



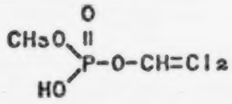
1-Hydroxy-2,2,2-trichloroethyl-dihydrogen phosphonate

Doubly demethylated trichlorfon



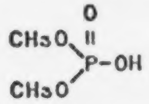
O,O-Dimethyl-*O*-(2,2-dichlorovinyl)phosphate

DDVP



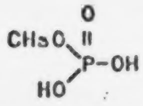
O-Methyl-*O*-(2,2-dichlorovinyl)hydrogen phosphate

Desmethyl DDVP



O,O-Dimethyl phosphate

DMP



Methyl phosphate

Mono methyl phosphate MMP, MP

Figure 1. Plant Metabolites of Trichlorfon and Dichlorvos

TABLE 1. RESIDUE OF TRICHLORFON ON FOLIAGE AND IN WATER AFTER AERIAL SPRAYING (1 LB/ACRE) BY DAY OF APPLICATION AND DAYS THEREAFTER. "WEST CREEK" TEST PLOT, PIKE NATIONAL FOREST, COLORADO (8)

Sample	Sampling Point	Day 0	Day 1	Day 7	Day 14
		ppm*			
Douglas-fir	10	8.6	3.0	1.3	0.3
Douglas-fir	11	11.8	7.1	0.5	<0.1
Douglas-fir	12	12.8	1.2	0.6	<0.1
Average	--	11.1	3.8	0.8	--
Willow	13	80.0	48.0	9.1	<0.1
Willow	14	70.7	37.9	1.9	0
Willow	15	53.0	34.9	2.5	0
Average	--	68.2	40.3	4.5	<0.1
Grass	16	44.1	22.8	4.6	2.1
Grass	17	57.6	47.3	5.4	1.9
Grass	18	27.7	19.8	5.4	<0.1
Average	--	43.1	30.0	5.1	<2.1

*Value of one measurement

75 ppm and 105 ppm to 5.93 ppm and 5.76 ppm, respectively, within one week (see Table 3). Residue levels in twigs and litter samples likewise decreased. At 106 days postspray some Dylox was still detectable in all of the samples analyzed. A follow-up analysis made 343 days postspray showed no measurable residues of Dylox in the forest soil and samples of current leaves (10). However, one twig sample showed a small residue, and Dylox residues were found in all forest litter samples (see Table 4). The levels of residue in litter, however, were considered too low to be of biological significance.

3.3 FATE IN SOIL

The fate of trichlorfon in the forest soil is determined by physical processes such as adsorption, leaching and runoff, and by chemical and

TABLE 2. RESIDUES OF TRICHLORFON ON FOLIAGE AND IN WATER AFTER AERIAL SPRAYING (1 LB/ACRE) BY DAY OF APPLICATION AND DAYS THEREAFTER. "LONG"TEST PLOT, PIKE NATIONAL FOREST, COLORADO (8)

Sample	Sampling Point	Day 0	Day 1	Day 7	Day 14
		ppm*			
Douglas-fir	1	22.4	13.5	1.5	0.8
Douglas-fir	2	6.5	12.4	2.2	0.4
Douglas-fir	3	8.8	5.3	1.5	0.8
Average	-	12.6	10.4	1.6	0.67
Willow	4	121.2	90.9	7.3	0.2
Willow	5	87.1	80.8	4.0	0.0
Willow	6	36.9	6.6	0.5	0.0
Average	-	81.7	59.4	3.9	0.07
Grass	7	101.7	39.0	5.9	2.9
Grass	8	11.3	16.4	12.4	1.4
Grass	9	226.0	17.0	0.5	2.0
Average	-	113.0	24.1	6.3	2.1

*Value of one measurement

microbial degradation. Volatilization and photodecomposition are probably less important because of the low volatility of trichlorfon and minimal light penetration through the litter layer. Based on the data supplied to EPA by the manufacturer on the persistence of trichlorfon in various soil types, half-life values are generally less than 30 days, with most of the values below 6 days (7).

3.3.1 Adsorption, Leaching, and Runoff

Information supplied to EPA by the manufacturer (7) indicates that trichlorfon is reversibly adsorbed on soil. The extent of adsorption (and hence, leachability) is dependent on soil type, with high organic soils exhibiting greatest trichlorfon retention capacity. Table 5 shows the

TABLE 3. SUMMARY OF DYLOX RESIDUES IN LEAF, TWIG AND FOREST LITTER SAMPLES (9)

Days Postspray	$\bar{x}$ ppm Dylox ± Standard Deviation					
	Leaves		Twigs		Litter	
	Ward Poundridge Reservation					
1	75.0	± 51.7*	1.73	± 1.09	5.14	± 4.52
2	56.7	26.7	1.44	0.94	7.65	7.55
3	34.8	27.5	1.26	0.56	2.85	2.46
4	19.4	14.3	1.33	0.80	3.20	2.87
5	9.57	5.09	1.60	0.63	4.72	3.96
7	5.93	4.87	1.59	0.91	2.14	1.59
16	1.39	1.66	0.93	0.89	1.13	0.64
28	2.24	1.66	0.93	0.89	1.13	0.64
106	0.73	0.90	0.02	0.04	0.04	0.07
	Blue Mountain Reservation					
1	105.0	121.0	3.10	1.99	6.21	7.03
2	43.4	28.2	1.27	0.67	7.44	6.32
3	33.6	28.8	1.12	0.55	3.60	4.67
4	13.0	8.77	2.84	1.17	9.75	9.10
5	9.49	5.21	3.29	1.97	13.7	11.6
7	9.49	5.21	3.29	1.97	13.7	11.6
16	0.91	0.73	0.70	0.26	6.32	3.96
28	1.90	1.66	0.66	0.24	1.38	1.31
106	1.20	1.57	0.05	0.04	0.08	0.10

* Each figure represents the average residue level from 9 sample stations on a specific date postspray.

adsorption coefficients and the estimated amounts of rainfall which would be required to leach trichlorfon 12 inches into three different soils tested in the laboratory. As shown in the table, the organic silt loam has the highest adsorption coefficient and requires the largest volume of water for leaching.

TABLE 4. SUMMARY OF DYLOX RESIDUE DATA FOR FOREST SAMPLES COLLECTED 343 DAYS POSTSPRAY FROM BLUE MOUNTAIN RESERVATION SPRAY PLOT (10)

Sampling Station	PPM Dylox			
	Forest Soil	Leaves	Twigs	Forest Litter
1	NM*	NM	0.13	0.81
2	"	"	NM	0.36
3	"	"	"	0.12
4	"	"	"	1.18
5	"	"	"	0.24
6	"	"	"	0.38
7	"	"	"	0.20
8	"	"	"	0.46
9	"	"	"	0.40
			$\bar{X}$ =	0.46
Control	NM	NM	NM	NM

* NM = nonmeasurable peak, equivalent to less than 0.05 ppm.

TABLE 5. TRICHLORFON ADSORPTION AND LEACHING FOR THREE SOILS (7)

Soil Type	pH	Adsorption Coefficients	Inches of Water Required for Leaching to a Depth of 12 in.
Sandy Loam	6.4	0.25	17.4
Silt Loam	5.5	0.40	22.2
Organic Silt Loam	5.4	0.51	25.1

Because of its high water solubility, trichlorfon is subject to leaching and washout from soil. The runoff tendency of trichlorfon in leachate was evaluated in a study where Dylox (4 lbs/gal) was sprayed on sloping plots of three soil types (sandy loam, silt loam, and high organic silt loam) (7). Application was made at 20 lbs/a.i./acre followed by simulated rainfall applied once a week for 5 weeks. After the 5-week period, total residues in the runoff water was analyzed. The amounts of trichlorfon found in the runoff as percentages of the quantity applied were 2.86 percent, 0.65 percent and 0.35 percent for silt loam, sandy loam and high organic silt loam, respectively. These results thus confirmed the adsorption results which indicated a higher trichlorfon retention capacity for soils high in organic matter.

3.3.2 Degradation

Trichlorfon is subject to degradation in soil. The rate of degradation appears to depend on soil characteristics, including pH. Degradation is considerably more rapid in alkaline soils than in acid soils (11).

Trichlorfon-1-^{14}C was incubated with wet sandy loam, grey, red and high organic silt loam soil under aerobic and anaerobic laboratory conditions. The most important factor contributing to degradation was soil pH. The half-life in pH 5.3 sandy loam soil was 11 days, while in pH 6.2 soil, it was one day.

Conflicting data have been reported regarding chemical vs. microbial routes for the degradation of trichlorfon in soil. In one laboratory study trrichlorfon degradation was found to be the same in sterile and non-sterile soils (see Table 6). Other studies (7,12) indicate that trichlorfon degradation in soil is primarily due to microbial action, with the extent of degradation depending on the species. One study (12) reported that at a trichlorfon content of 0.1 to 12.5 mg/ml, 100 percent of the preparation was decomposed; 92 percent of the degradation was attributed to microorganisms and only 8 percent to chemical reactions. At higher concentrations, the trichlorfon was degraded more slowly. Sterilization of silty loam soil has been shown to double the half-life of trichlorfon while 1 percent sucrose added to the soil increased the rate of breakdown, indicating the role of microorganisms in trichlorfon metabolism (7). In this study, the only

TABLE 6. TRICHLORFON DEGRADATION IN STERILE AND NON-STERILE SOILS (11)

Concentration (in mg/kg)	Soil	Sampling Period Initial	After 20 Days	After 30 Days	After 40 Days
100	Nonsterile	123.0	22.0	5.6	0.52
100	Sterile	123.0	21.6	5.8	0.59
10	Nonsterile	13.0	5.0	1.04	0
10	Sterile	13.0	5.0	1.22	Traces

metabolic products detected in soil were hydrolytic products resulting from P-O-CH_3 rupture.

A laboratory study on forest soils (9), performed at the State University College of Forestry at Syracuse University indicated that Dylox degrades rapidly in soil (see Table 7). Detectable residues dropped rapidly from the initial concentration unit. After 13 days, only soil cultures treated with 10 ppm Dylox retained any measurable residues. No DDVP was detected in any of the samples examined.

TABLE 7. RESIDUES DETECTED AT VARIOUS PERIODS OF TIME FROM SOIL SAMPLES TREATED WITH KNOWN CONCENTRATIONS OF DYLOX (ANALYTICAL GRADE) (9)

Days after treatment	Initial Dylox Concentration 0 (Control)	1 PPM	5 PPM	10 PPM
0	< 0.05 ppm*	0.68 ppm	6.00 ppm	10.60 ppm
3	< 0.05 ppm	0.20 ppm	2.19 ppm	2.84 ppm
6	< 0.05 ppm	< 0.05 ppm	0.81 ppm	1.85 ppm
9	< 0.05 ppm	< 0.05 ppm	0.50 ppm	0.65 ppm
13	< 0.05 ppm	< 0.05 ppm	< 0.05 ppm	0.30 ppm

* Sensitivity of analytical procedures: 0.05 ppm.

3.4 PERSISTENCE IN WATER

The available data indicates that trichlorfon breakdown in natural water is relatively fast. The breakdown rate is higher under alkaline pH conditions and at warmer temperatures. Mobay reports that the half-lives of Dylox in water in the dark at 30°C at pH 5, 7 and 9 are 4.7, 0.6 and 0.1 days, respectively (13). The corresponding half-lives at 50°C are 3.7, 0.2 and 0.03 days, respectively. Dylox in an outdoor pond (pH 7, average temperature 29°C, and exposure to sunlight) showed a half-life of only 0.3 days (7). A laboratory study performed by McGill University on the chemical stability of trichlorfon in fresh and salt water concurs that in acidic fresh water, trichlorfon is relatively stable and may persist long enough to be absorbed into various levels of the food chain; in contrast, trichlorfon is unstable in sea water and is readily degraded (14).

The persistence of trichlorfon in forest waters was evaluated in a study at the State University College of Forestry at Syracuse University (9). Several forest plots were sprayed with Dylox (1 lb/acre) without any precaution to avoid direct spraying of the lakes and streams in the study plots. Dylox residue levels in water samples ranged from 0.40 to 0.06 ppm one hour after spraying and decreased to a non-detectable level (less than 0.002 ppm) after 4 days (see Table 8). There were no detectable residues in any of the mud samples indicating that Dylox does not concentrate in lake and stream bottom sediments.

TABLE 8. DYLOX RESIDUES IN LAKE AND STREAM WATER SAMPLES (9)

		PPM Dylox in Water				
Sampling Interval	Sampling Site:	Lake	Lake	Lake	Stream	Stream
Prespray		ND*	ND	ND	ND	ND
1 Hour		0.400	0.100	0.062	0.084	0.060
1 Day Postspray		0.071	0.041	0.085	0.034	0.036
2 Days Postspray		0.022	0.016	0.061	0.020	0.010
3 Days Postspray		0.006	0.006	0.005	0.042	0.023
4 Days Postspray		0.002	0.002	0.004	0.002	0.004
5 Days Postspray		ND	ND	ND	ND	ND
7 Days Postspray		ND	ND	ND	ND	ND
16 Days Postspray		ND	ND	ND	ND	ND

* ND = Not detectable; less than 0.002 ppm.

Analysis for DDVP (a Dylox metabolite) residues indicated that several of the water samples contained small amounts of DDVP (see Table 9).

TABLE 9. DDVP RESIDUES IN WATER (9)

Sample	Sampling Site	Sampling Interval	PPM DDVP
Water	Lake	1 Hour	0.010
Water	Lake	1 Day Postspray	0.007
Water	Stream	2 Days Postspray	ND*
Water	Stream	3 Days Postspray	0.002
Water	Stream	4 Days Postspray	ND
Water	Stream	5 Days Postspray	ND
Water	Stream	7 Days Postspray	ND

*Not detectable; less than 0.002 ppm for water.

4.0 IMPACTS ON NON-TARGET ORGANISMS

4.1 IMPACTS ON AQUATIC ORGANISMS

Laboratory acute toxicity data indicate that trichlorfon is highly toxic to certain aquatic organisms, particularly to some aquatic invertebrates (Table 10). Field evaluations of the effects of trichlorfon on aquatic insects also indicate that trichlorfon can be lethal to certain species (e.g., stoneflies and Collembola) even at the recommended application rate of 1.0 lb/acre (4).

Trichlorfon is less toxic to fish than to invertebrates (Table 10). In fact, some fish parasites have been treated with trichlorfon. One trichlorfon formulation, Masoten, is registered for the control of fish parasites at a recommended application rate of 0.5 lb trichlorfon/acre-ft of water (4). Dylox has also been tested as a control for fairy shrimps in fish hatchery ponds. It is highly toxic to fairy shrimp at levels of 0.10 and 0.25 mg/L; mortality exceeded 82 percent in 48 hours in laboratory tests.

In studies exposing rainbow trout and eastern brook trout to continuous applications of 1 ppm and 10 ppm, respectively, there were no effects observed after 24 and 72 hours of exposure (7), but rainbow trout exposed to

TABLE 10. ACUTE TOXICITY OF TRICHLORFON TO AQUATIC ORGANISMS (7)

Species	Toxicant	Effect
Bluegill (Lepomis macrochirus)	80% dust	24-hr LC_{50}=95 ppm
		48-hr LC_{50}=22 ppm
		96-hr LC_{50}= 4 ppm
Rainbow trout (Salmo gairdneri)	80% dust	24-hr LC_{50}=6.0 ppm
		48-hr LC_{50}=2.55 ppm
		96-hr LC_{50}=1.22 ppm
		96-hr LC_{50}=1.8 ppm
Rainbow trout	Technical	96-hr LC_{50}=4.8 ppm
Striped bass (Roccus saxatilis)	50% soluble powder	24-hr LC_{50}=10.4 ppm
		48-hr LC_{50}=9.2 ppm
		96-hr LC_{50}=5.2 ppm
Fathead minnow (Pimephales promelas)	99% Technical	96-hr TLM=110 ppm
Goldfish (carassius auratus)	"	24-hr TLM-1000 ppm
		48-hr TLm-320 ppm
		96-hr TLm=100 ppm
Bluegill	Neguvon* 8% liquid	24-hr LC_{50}=>52 ppm
	Dylox 50% powder	24-hr LC_{50}=41 ppm
	99% Technical	24-hr TLm=12 ppm
		48-hr TLm - 7.2 ppm
		96-hr TLm - 3.8 ppm
Guppies (Lebistes reticulatus)	"	24-hr TLm=120 ppm
		48-hr TLm=23 ppm
		96-hr TLm=7.2 ppm
Stonefly (Pteronarcella badia)	Not Specified	24-hr LC_{50}=0.050 ppm
		48-hr LC_{50}=0.022 ppm
Amphipod (Gammarus lacustris)	Not Specified	24-hr LC_{50}=0.092 ppm
		48-hr LC_{50}=0.060 ppm
Waterflea (Daphnia pulex)	Not Specified	48-hr LC_{50}=0.18 ppb
(D. magna)		48-hr LC_{50}=0.0081 ppm
Pink shrimp	Not Specified	24-hr EC_{50}=0.44 ppm
		48-hr EC_{50}=0.36 ppm

*Neguvon is used for control of cattle grubs and lice (5).

10 ppm for 24 hours did not survive. However, a level of 10 ppm is much higher than levels expected from forest spraying. Field investigations of the impact of trichlorfon on aquatic organisms in forest waters have indicated little adverse effects on fish when Dylox is applied at the recommended application rate of about 1 lb/acre (4).

Dylox also does not appear to bioaccumulate in aquatic species. In one postspray field investigation of trichlorfon residues in fish tissue, residue levels peaked 12 and 24 hours after a 1.0 lb trichlorfon/acre application and were at or below detectable limits (<0.02 ppm) after 96 hours, thus indicating that trichlorfon was eliminated and not bioaccumulated (4). In another field study (9), Dylox was aerially applied at the rate of 1.0 lb/acre over forest plots including lakes and streams. No Dylox residues were detected in fish or snake samples; however, a small residue was found in one frog sample taken one day postspray (see Table 11). No residues were found in frog samples taken 3 days postspray. In rooted aquatic plant samples, Dylox residues were found through the 28th day postspray, but not detected at 106 days.

In tests for residue accumulation in fish, bluegill and catfish were exposed to trichlorfon at a concentration of 1 ppm in the water (7). Maximum residue in edible flesh was 0.02 ppm in samples taken 4 hours after the last of four applications at 7-day intervals. Samples taken 20 hours later contained <0.01 ppm.

4.2 IMPACTS ON SOIL MICROORGANISMS

As noted previously, microbial degradation is believed to be a major factor in the degradation of trichlorfon in soil. One laboratory study using various cultures of soil bacteria and fungi indicated that trichlorfon at concentrations of 1, 5 and 10 ppm had no apparent effect on the population of microorganisms (see Table 12) (9).

In another study (7), clay loam and silt loam soils were treated with trichlorfon at 50 and 250 mg/kg and maintained at 50 percent field moisture capacity for 56 days. No effect was noted on populations of fungi, bacteria, or actinomycetes due to treatment.

TABLE 11. DYLOX RESIDUES IN VARIOUS AQUATIC ORGANISM SAMPLES (9)

Sample	Sampling Interval (Days Postspray)	PPM Dylox
Fish*	Prespray	ND‡
Fish	3	ND
Fish	78	ND
Frogs	Prespray	ND
Frogs	1	0.06
Frogs	3	ND
Water Snake	3	ND
Rooted Aquatics†	Prespray	ND
Rooted Aquatics	1	0.24
Rooted Aquatics	3	0.33
Rooted Aquatics	28	0.05
Rooted Aquatics	106	ND

* Composites of small blue gills (Lepomis macrochirus).

† Composite of arrow arum (Peltandra cf. virginica).

‡ ND - not detectable; less than 0.05 ppm.

4.3 IMPACTS ON NON-TARGET INSECTS

Trichlorfon will reduce populations of some non-target insects even at recommended application rates. Adverse effects on various insect species have been reported as a result of trichlorfon treatment for the control of gypsy moth and spruce budworm (16). In Connecticut, flesh flies, Tacinidae and true bugs were reduced by 90 percent after trichlorfon treatment. True flies, ants, wasps, moths and butterflies were reduced after trichlorfon treatment in New York. In Maine, reduced populations of spiders, gnats, butterflies and tachinids were reported.

Available data indicate that trichlorfon is relatively non-toxic to honey bees. One study indicated that bees caged with trichlorfon treated foliage (sprayed 2 hours previously) sustained only 7 to 18 percent mortality (4). Trichlorfon residues are not expected to be transported by foraging bees from contaminated surfaces into hives (4). The toxicity to honey bees

TABLE 12. NUMBERS OF MICROORGANISMS PER GRAM OF SOIL AT VARIOUS PERIODS OF TIME AFTER TREATMENT WITH KNOWN CONCENTRATIONS OF DYLOX; DILUTIONS PLATED ON 3 MEDIA (9).

Initial Dylox conc.	Days after treatment	N.A.[†] Bacteria	Microorganisms/gram of soil[*]			Total
			N.F. Bacteria	Bacteria	P.G.A. fungi	
0 ppm (Control)	0	128	96	9	15	24
	3	272	212	515	85	600
	6	148	89	126	40	166
	9	261	84	247	20	267
	13	303	92	245	46	291
1 ppm	0	126	76	19	14	33
	3	197	80	3	30	33
	6	189	91	142	44	186
	9	275	79	392	21	413
	13	333	--	217	13	230
5 ppm	0	146	89	680	70	750
	3	317	155	278	42	320
	6	145	139	93	44	137
	9	181	67	222	41	263
	13	271	88	359	122	481
10 ppm	0	117	68	43	18	61
	3	202	157	195	58	253
	6	223	77	205	34	239
	9	164	74	275	22	297
	13	381	88	259	53	312

[*] Actual populations are table values x 10^4, except for bacteria on nitrogen-free agar medium which are x 10^5. Soil pH: 6.8.

[†] N.A. - nutrient agar; N.F. - nitrogen-free agar; P.G.A. - peptone glucose acid agar.

has been measured in laboratory studies with an LD_{50} of 59.83 μg/bee, a level considered to be relatively non-toxic (17).

4.4 IMPACT ON BIRDS

No bird mortality has been observed in field observations following application of trichlorfon at a rate of 1 lb/acre (19,20). However, trichlorfon may induce certain subacute effects in birds such as depression of brain cholinesterase levels. Such depression has been used as an indicator of organophosphate poisoning. Passerine bird species were analyzed for brain cholinesterase levels following spraying of 1.13 kg/ha of trichlorfon in forest plots in southwestern Montana (21,22). Sufficient data were obtained from 10 species to evaluate the effects of trichlorfon on brain cholinesterase activity. One dark-eyed junco, one evening grosbeak, two mountain chickadees, and two western tanagers had values which were at least 2 standard deviations below the mean. The western tanagers collected on the day of spraying had depressed brain cholinesterase activities 21 percent and 27 percent below the mean. The evening grosbeak (collected on day 3) had 19.7 percent inhibition.

In another study (20), trichlorfon was applied to forests in southwestern Montana at a rate of 1 lb a.i. in 1 gallon per acre. No significant decrease in bird numbers was detected based on breeding-pair estimates and live bird counts after spraying. No sick or dead birds were found and the success of nests in sprayed plots did not differ significantly from those of the control plots.

Messick, et al. (19) found that trichlorfon applied at recommended application rates does not cause major pheasant losses in southwestern Idaho. Observations on penned and radio-equipped wild pheasants within the treatment area revealed no direct mortality from spraying. Penned pheasants 5 to 15 days old exhibited symptoms of organophosphorus poisoning, but recovered. Crop analysis indicated that pheasants in the treated area consumed significantly fewer insects than those birds in the control area, probably due to decreases in insect availability as a result of spraying.

Songbirds collected from areas sprayed with trichlorfon at a rate of 1 lb/acre in eastern Pennsylvania contained low, but detectable levels of trichlorfon (23). The amounts found were 0.001 ppm in a blue jay, 0.003 to

0.01 ppm in crested flycatchers, and 0.005 to 0.04 ppm in Baltimore orioles. These residues are considered to be very small and, in most cases, are within the USDA allowances for residues in beef (0.1 ppm), milk (0.01 ppm), and many vegetables (0.1 ppm).

Toxicity data is available for some bird species to trichlorfon. In bobwhite quail, the LD_{50} is 500 mg/kg in feed (7). A level of 25 ppm in the diet has been found to reduce reproduction by 25 percent. For ringnecked pheasant, an oral LD_{50} of 25 mg/kg in feed has been determined (7). Acute oral LD_{50} values of 28 to 50 mg/kg and 38 to 50 mg/kg have been reported for redwinged blackbirds and starlings, respectively (7).

4.5 IMPACTS ON MAMMALS

Toxicity of trichlorfon to mammals has been studied since it is used in veterinary practice to kill pests on animals. In one study (24), sheep were given 3 or 10 percent aqueous solutions of trichlorfon. Animals received levels up to 0.2 g/kg. A slight increase in body temperature as well as an increase in the number of leukocytes was noted. The highest blood level reached was 2 mg/kg, 1-2 hours following administration. After 6 hours, only trace levels remained in the blood and none was detected after 30 hours. Histologic studies of the liver, kidney and cardiac muscle revealed minor effects which were reversible.

In a cow treated orally with trichlorfon and a dog injected with trichlorfon, most of the chemical was metabolized and excreted in the urine (7). Among the reported metabolites in mammals are DDVP, trichloroethylglucuronide, dimethyl phosphate, monomethyl phosphate, demethylated trichlorfon, 2,2,2-trichloro-1-hydroxyethyl phosphate, methanol, formic acid, and CO_2.

Table 13 presents the toxicity data reported by Mobay Chemical Corp. for various trichlorfon formulations.

There have been reports that trichlorfon may be teratogenic in mammals. One study has indicated that trichlorfon is teratogenic in rats at doses of 432 or 519 mg/kg (4). Another study has indicated embryotoxic and teratogenic effects in rats from an 80 mg/kg dose (4).

In field studies, depressed brain cholinesterase activity has been observed in the white-footed mouse following an application of 1.0 lb/acre

TABLE 13. TOXICITY DATA FOR VARIOUS TRICHLORFON FORMULATIONS (1)

Formulation	Species	Sex	Oral LD_{50}, mg/kg	Dermal LD_{50}, mg/kg	Inhalation LC_{50}, µg/1/60 min
Technical	Rat	M	184	>2,000	>10,000
		F	144	>2,000	
	Rabbit	M		>2,100	
80% soluble powder	Rat	F	Approx. 470	>2,000	>20,000
1.5 oil	Rat	F	2,500	>2,000	
Liquid solution	Rat	F	950	>2,000	
5% granular bait	Rat	M			>20,000
		F			>20,000

of trichlorfon (4).. In other studies, however, no impacts on small mammals have been observed (4). One study reports that inhibition of mammalian cholinesterase is caused by the dichlorvos formed from trichlorfon (25).

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III. BIOLOGICALS

Common Name:	Bacillus thuringiensis
Chemical Name:	Bacillus thuringiensis Berliner
Major Trade Names:	Dipel; Thuricide
Major Applications in Forestry:	Bacillus thuringiensis is used primarily in the Northeast forests for control of the spruce budworm in areas where chemical insecticides cannot be used.

SUMMARY

Bacillus thuringiensis (B.t.) is a microbial insecticide that is particularly effective in controlling a number of insect species of the order Lepidoptera. B.t. is formulated as a suspendible powder which is applied as a water-based aerosol. The active ingredients of B.t. preparations are bacterial spores, which infect tissues of sensitive insects, and a crystalline protein toxin, which becomes active only in the gut of insects with alkaline pH and the proper digestive enzymes.

There is limited data available on the fate of B.t. in soil and water. However, the available studies indicate that the spores of B.t. may persist in the soil for at least several months. Viable spores of B.t. are not expected to persist in water for longer than one month. The primary cause of inactivation of the spores in the environment is probably sunlight. The susceptibility to solar radiation is enhanced under humid conditions.

In field tests of B.t., no adverse effects on mammals, birds, fish or on beneficial insects have been observed. In laboratory tests, B.t. has toxic effects on a few beneficial invertebrates and vertebrates, but these effects occur only at levels far higher than those achieved under field conditions of application. Furthermore, B.t. has never been reported to cause disease in man or in other vertebrates.

1.0 INTRODUCTION

Bacillus thuringiensis (B.t.) is a naturally-occurring bacterium which is pathogenic to a number of insect species primarily in the order Lepidoptera. All bacteria in the genus Bacillus form endospores which are a dormant stage in the life cycle. Endospores are highly resistant to both heat and dessication. Therefore, they can persist for long periods when the environment is unfavorable for bacterial growth. The spores in these rod-shaped bacteria are formed several hours after vegetative growth slows and cells enter the stationary phase. The mature spores are oval bodies located either centrally or sub-terminally within the parent cell, the sporangium. A distinctive feature of Bacillus thuringiensis is the presence of a bipyramidal crystal, the parasporal body, within the sporangium. This crystal, which has been called "delta-endotoxin", is the principal active ingredient of B.t. insecticide formulations. Endospores constitute the second active ingredient of B.t. formulations.

B.t. was first isolated in Japan in 1901 from diseased larvae of the silkworm (2) and reisolated in 1911 from diseased larvae of the Mediterranean flour moth (3). The first commercial use in the U.S. occurred in 1958 when application of the B.t. formulation, Thuricide, directly to food and forage crops under the conditions of a temporary exemption from a tolerance was authorized. Since that time, B.t. use has expanded to include forest pests. The cumulative total acreage aerially sprayed in the U.S. between 1958 and 1974 for suppression of forest insect populations was 23,000 acres (4). In recent years, B.t.'s major use in forestry has been for spruce budworm control in Maine. B.t. was applied to about 200,000 acres during the 1980 spray program in Maine (5).

Independent isolations of B.t. have produced a number of varieties or strains of this bacterium that differ in their pathogenic properties as well as in their serological reactions. Early formulations of B.t. manufactured in the U.S. were produced from B. thuringiensis var. thuringiensis and contained a second toxin called "beta-exotoxin" which has a broad range of toxicity to insects including honey bees (7,8). However, damage to bees occurs only at application rates much higher than the recommended rates. All B.t. formulations currently manufactured in the U.S. are produced from strain kurstaki (HD-1) which was selected by Dulmage (9) for its high virulence to target lepidoptera. This strain is not toxic to honey bees nor does it produce beta-exotoxin.

In the U.S., the potency of B.t. preparations is defined in terms of International Units by a standardized bioassay that determines the potency of the preparation relative to the potency of a standard preparation, HD-1-S-1971, derived from the commercially used strain HD-1 with a determined potency of 18,000 IU/mg (10). All preparations of B.t. sold in the U.S. are required to list the number of International Units on their labels.

B.t. is usually applied as a suspension in a water-based formulation. Spray formulations generally contain additives designed to increase their effectiveness. Among these additives are thickening agents to keep the spores, parasporal crystals and other ingredients in a uniform suspension; wetting agents to obtain better leaf coverage; antievaporants; stickers to increase the retention of spray deposits on foliages; and protectants to reduce the adverse effect of solar radiation on the spores and crystals (11). Field tests have been performed for many years on a variety of formulations to determine their effectiveness against forest insect pests. Selected examples of these experiments are described in Table 1.

The major producers of B.t. in the U.S. are Abbott Laboratories (for Dipel) and Sandoz Inc. (for Thuricide). There are also foreign producers which market B.t. in the U.S. under a variety of trade names: Bactospeine, Leptox, Novabac, Bug Time, and Cekubacilina (18). For forest use, B.t. is generally aerially applied. Typical application rates for the gypsy moth are 2 quarts of Dipel LC per acre or 1/2 to 1 lb of Dipel worm killer in 1 to 5 gallons of water (19). Thuricide 16B and Dipel 4L for the spruce budworm are applied at a dosage of 8 Billion International Units (BIU) per acre (20).

2.0 PROPERTIES AND MODE OF ACTION

Bacillus thuringiensis belongs to a genus of rod-shaped spore-forming bacteria that grow aerobically or facultatively anaerobically. Its vegetative cells are approximately 1 µm in width and 5 µm in length (21). They are motile and are propelled by peritrichous flagellae. B.t. can grow in moist soils deriving nutrients from decaying plants and can grow in the tissues of infected insects. Several hours after vegetative growth stops

TABLE 1. FIELD TESTS OF B.t. AGAINST SOME FOREST INSECTS

Host	Test Area	Formulation/Dose Applied	Results	Reference
Thyridopteryx ephemeraeformis (bagworm)	2 acres of Scotch Pine in Missouri	Dipel WP having at least 25 billion viable spores/gm in a solution of 6 gal water plus 2 qts. crude molasses applied at 0.5 lb/acre.	95% reduction in the bagworm population	13
Forest tent caterpillar	Each formulation was applied to a 20-acre plot of water tupelo swamp forest in Alabama	Dipel WP, 0.25 lb/acre Dipel WP, 0.50 lb/acre Thuricide HPC, 1 qt/acre	35-40% average foliage loss 30-35% average foliage loss 40-50% average foliage loss 27 days after treatment. The control plot had 95-100% foliage loss	14
Douglas fir tussock moth	20-acre plots in Wallowa-Whitman National Forest in Oregon	Dipel WP in a 25% molasses solution applied at 1 lb/acre to the 2nd or 3rd instar.	The population reduction exceeded 95% at 35 days. Defoliation levels were below 25%	15
Choristoneura fumiferana (spruce budworm)	Two 100-acre plots of balsam-fir in Quebec	Thuricide HPC Thuricide HPC + chitinase*	85% larval mortality 93% larval mortality The control plot had 54% mortality.	17
Choristoneura fumiferana (spruce budworm)	10,000 acres of balsam-fir forest in Quebec	Thuricide HPC + chitinase in a formulation containing adjuvant and sticker applied at .005 to 1.33 gal/acre	In areas where the spray deposit was >0.4 gal/acre and the plate counts were >77 colonies/cm^2 for B.t., the average mortality was 88.2%	16
Lymantria dispar L. (gypsy moth)	Two 500 acre plots of eastern hardwoods in Pennsylvania	Thuricide 16B and Dipel LC at 8 BIU/acre	80-90% larval reduction and 92% foliage protection	12
Paleacrita vernata (spring cankerworm); Alsophila pometaria (fall cankerworm)	Windbreaks in North Dakota	Biotrol WP at 3.4 BIU/acre; Dipel LC at 4.0 BIU/acre; Thuricide 16B at 4.0 BIU/acre	85-95% larval reduction	12

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*Chitinase has been shown to accelerate development of disease probably by disruption of the chitinase lining of the gut lumen which would allow better contact of ingested spores with cells of the gut wall and facilitate penetration (16).

and cells enter the stationary phase, the process of sporulation begins. The first step is the appearance in the cell of a relatively transparent forespore which gradually changes into the mature spore. The process of spore maturation is accompanied by the development of the parasporal crystal. Eventually, the sporangium, the cell containing an endospore and parasporal crystal, lyses.

B.t. must be ingested by susceptible insects before it can kill. This normally occurs when larvae feed on foliage sprayed with B.t., thereby ingesting both endospores and parasporal crystals. The crystal is comprised of a protein that is insoluble at acidic or neutral pH but is soluble at alkaline pH. Those insects that are most susceptible to B.t. have alkaline gut contents between pH 9.0 and 10.5 (1). The solubilized protein must be cleaved by digestive enzymes to form the active toxin which works by attacking the gut lining of epithelial cells. This allows molecules in the alkaline gut to diffuse into the hemolymph, increasing the pH of tissues and resulting in paralysis (1,22). When the epithelial gut lining has been sufficiently damaged, ingested spores can pass into the hemolymph and germinate. Here, the bacteria grow vegetatively, producing a fatal septicemia. Sporulation begins after growth stops and leads to production of endospores and parasporal crystals within dead insect tissues.

In highly susceptible insects, only the toxin is needed for control, but in less susceptible insects, the synergistic effect of endospores together with toxin is required. Since the chitinous layer in the insect gut is the main barrier that B.t. must pass through in order to invade tissues, some investigators have added chitinase, an enzyme that hydrolyzes chitin, to B.t. formulations. This approach appears to increase the virulence of B.t. preparations in laboratory tests (23) but, despite various field tests (42,43) addition of chitinase has not been universally accepted as beneficial for field use.

3.0 ENVIRONMENTAL FATE

Most studies of the persistence of B.t. in the environment have been directed at following viability of B.t. spores rather than following toxin activity. This is primarily because the presence of the crystal in nature is much more difficult to detect than is the presence of spores. Those studies that have been carried out to follow persistence of the crystalline toxin show that it disappears from the environment at a steady rate, although somewhat slower than the disappearance of B.t. spores (24).

B.t. spores and vegetative cells occur naturally in a number of environments not contaminated by B.t. insecticide formulations. This organism is commonly found where susceptible insects inhabit the environment. For example, it is frequently found in stored grain and in the soils of environments with high concentrations of lepidopterous larvae (24).

When B.t. is applied in nature, the spores rapidly disappear. The primary cause of inactivation of B.t. spores in the environment is probably sunlight, although endospores are generally resistant to heat, shortwave radiation, and toxic chemicals. It has been shown that moist, unprotected spores of B.t. are rapidly killed by exposure to sunlight (26). Further studies also suggest that spores exposed to sunlight are less susceptible to solar radiation damage under very dry conditions (25). When four commercial B.t. preparations were sprayed on coast live oak at different locations, the viable spores persisted longer in the hot, dry climate than in the cool, moist climate. In another study, the persistence of four B.t. formulations was tested on redbud tree leaves at two sites in California: Auburn (altitude, 374 m) and Sacramento (altitude, 10 m) (27). The rate of decay of viable spores was not significantly different although the amount of solar radiation was greater at Auburn. It was concluded that since the relative humidity at Auburn was lower (21.7 percent vs. 27.5 percent), the drier conditions may have compensated for any difference in solar radiation levels.

Sunlight and humidity are probably not the only factors affecting the persistence of spores on vegetation. It has been suggested that the initial B.t. deposit retained on the leaves after application and the subsequent decay or loss of viable spores may be determined to some extent by the leaf type or species, based on studies measuring viable spore decay on the leaves of four different species of trees (California live oak, redbud, eucalyptus, and walnut) subject to the same climatic conditions (28).

It is generally recognized that endospores can remain dormant for a long period of time, in some cases for many years. B.t. has been known to remain active in soil for at least four months (29). In laboratory studies evaluating some of the factors affecting the survival and competitive growth of B.t. in soil, Saleh, et al. (30) confirmed that spores of B.t. can remain viable for long periods of time in soil when germination-inducing stimuli are absent. Under conditions favorable for the growth of soil bacilli, such as neutral pH and presence of proteinaceous matter, B.t. can germinate and compete in the vegetative phase with other soil microorganisms. B.t. can also sporulate successfully to levels of more than 1 million spores/g soil.

Although few studies are available on the fate of B.t. in water, one study suggests that B.t. will not persist in aquatic systems based on data collected from monitoring river water following aerial applications of Thuricide to forest plots in Canada (31). The viable spores present in river water and clams immediately after treatment disappeared within four weeks.

4.0 IMPACTS ON NON-TARGET ORGANISMS

4.1 IMPACT ON TERRESTRIAL INVERTEBRATES

Regardless of the persistence of B.t. in the environment, non-target invertebrates are not expected to be harmed by exposure to B.t. at levels commonly encountered after spraying of forests. In field tests in Nova Scotia where B.t. was the only insecticide applied to an apple orchard over a four-year period, population levels of lepidopteran insects were reduced but there was no effect on predaceous insects (32).

Spruce-fir stands in Algonquin Park, Ontario (Canada) and mixed forest containing mature spruce stands, poplar bluff, and areas of dense brush and open fields in Spruce Woods, Manitoba, were sprayed with formulations of Thuricide 16B or Dipel WP. Although some declines in populations of non-target insects were observed, comparison with the controls indicated that the declines would not be attributed to the spraying (31). In these studies, there was also no significant increase in mortality among foraging bees as a result of B.t. treatment. Many other studies have been made on the effects of B.t. on honey bees (7,8,33,34,35,36). These studies have found no evidence that bees will be harmed by B.t. at the levels commonly used in spray operations. B.t. has been shown to be non-toxic to bees at levels as high as 726,000 spores per bee (37).

One study has shown B.t. to be fatal to earthworms at concentrations 10^4 to 10^5 times higher than that which would occur in the soil after normal application in the field (39). However, these studies were carried out using B. thuringiensis var. thuringiensis that produces beta-exotoxin which could have influenced the results. In experiments using Dipel (16,000 IU/mg) at dose rates of 60, 600, and 6,000 mg/m^2 on forest plots and Bactospeine (1000 IU) at a dose rate of 30 g/m^3, worm density after spraying was not significantly different from worm density prior to spraying (38).

4.2 IMPACT ON AQUATIC SPECIES

Few toxic effects have been reported in studies on B.t. exposure to aquatic species. While monitoring aquatic species on Moresby Island, British Columbia in 1960, Todd and Jackson (40) found no adverse effects on Coho salmon fry or on aquatic insects in streams within an experimental area treated with B.t. In studies in Algonquin Park, Ontario, Canada, fish and bottom fauna suffered no adverse effects up to four weeks after spraying (31). Data from in vivo tests evaluating the safety of B.t. to fish (Table 2) show B.t. to be either non-toxic or toxic only at very high doses.

4.3 IMPACT ON MAMMALS AND BIRDS

Field tests have not revealed any deleterious effects of B.t. on populations of birds and mammals. In studies in Algonquin Park and Spruce Woods, no significant differences were found between the populations of birds and mammals on the sprayed plots vs. the populations on the untreated plots (31). In a second test, aerial application of Dipel WP applied at a rate of 0.5 lb/acre to a Scotch pine plantation containing a large population of nesting mourning doves apparently did not affect or disturb the birds (13). Twenty-four hours after spraying, fledglings were observed still in their nests and adults were flying about the plantation. After 28 days, adults were still numerous.

Extensive laboratory tests have produced no evidence that B.t. is pathogenic to vertebrates which inhale, ingest, or come into contact with it. Table 2 summarizes the results of some of these studies. Human volunteers inhaled 100 mg/day of Thuricide powder for 5 days with no adverse effects and ingested 1 gm/day for 5 days with no adverse effects (3). Rats were given a single oral dose up to 24 gm/kg of body weight without adverse effects. When mice were injected with large numbers of B.t. spores and cells (10^6-10^9), some individuals died. This appeared to be the result of

TABLE 2. SUMMARY OF IN VIVO TESTS CONDUCTED TO EVALUATE SAFETY OF BACILLUS THURINGIENSIS PREPARATIONS TO FISHES, BIRDS, AND MAMMALS (41)

Species	Numbers of Animals	Inoculum*		Results
		(billion/kg)	Route**	
Fishes				
Rainbow trout, black bullhead, yellow perch, mosquito fish	40	<0.01-4.5	TE	negative
Coho salmon juvenile	20	300-1800	TE	toxicity at higher doses
Birds				
Wild pheasant	9	3600	diet	negative
Partridge	2	5800	diet	negative
Cornish chick	190	0.2	diet	negative
Chick	48	300-1900	diet	negative
New Hampshire laying hen	16	1000-3000	diet	negative
Cockeral, Vantress cross	60	480-15,800	diet	negative
Mammals				
Mouse	48	0.1-0.3 cells	ip	lethal dose, 50%
	48	0.04-2 cells	sc	lethal dose, 50%
	48	0.8-7.8 spores	ip	lethal dose, 50%
	48	20-160 spores	sc	lethal dose, 50%
	10	77	po	negative
	10	15	ip	abdominal irritation; some death
	10	20,000	ih	negative
Rat	10	2000	po	negative
	100	7700	diet	negative
	20	0.01-1.0	ip	negative
Guinea pig	10	77	diet	negative
	10	40	ip	negative
	10	4000	ip	negative
	10	0.3	sc	localized reaction at injection site
	10	16	DA	slight erythema on abraded skin
Swine, duroc	3	185	diet	negative
Human	18	0.2	po	negative
	5	0.02	ih	negative

*Viable spore count of whole culture preparation that included spores, vegetative cells, crystals, and whole culture broth, unless otherwise specified. Estimated body weight was used when active body weight was not provided.

**po, per os; ip, intraperitoneal; in, inhalation; sc, subcutaneous, TE, topical exposure; DA, dermal application.

toxic substances in the B.t. preparations since death also occurred after injecting heat-killed preparations. No evidence of infection was seen, and bacteria completely disappeared from the blood by 72 hours after injection (3).

As a result of the widespread natural occurrence of B.t., there is certainly occasional human exposure to this organism through inhalation, ingestion, and wound contamination. However, there are no reports of human disease caused by B.t. Furthermore, no adverse effects of occupational exposure to Thuricide have been noted, nor have adverse effects been detected following its use (3).

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Common Name:	Nucleopolyhedrosis virus
Chemical Name:	Nucleopolyhedrosis virus
Major Trade Names:	Gypcheck; TM-Biocontrol-1
Major Applications in Forestry:	Nucleopolyhedrosis viruses are used as insecticides against specific forest insects. Current use is very limited.

SUMMARY

Nucleopolyhedrosis viruses (NPV's) are a group of naturally-occurring viruses that infect and kill a number of insects in the orders Hymenoptera and Lepidoptera. Each NPV is host specific, and NPV insecticides are formulated as a suspendible powder containing virus that is active against a single insect pest. NPV's are currently registered for use against several agricultural pests and are registered for use by the USFS against the gypsy moth and Douglas-fir tussock moth.

NPV's invade insect tissues after foliage contaminated with virus has been ingested, but the virus can also be transmitted transovarially. Tissues of insects killed by NPV contain large amounts of infectious virus which, in certain cases, can give some long-term pest control. However, NPV's are normally not persistent on foliage as they are inactivated within a few days when exposed directly to sunlight. Soil appears to be a natural reservoir for NPV's where they can persist, in some cases, for several years. Little is known about the fate of NPV's in water.

In field studies on the impact of NPV's on the environment, no adverse effects on non-target animal or plant species have been observed. This is undoubtedly due to the extreme host-specificity of these viruses. Furthermore, laboratory studies on fish and mammals exposed to NPV's in water, in food or by intraperitoneal injection have not revealed adverse effects. No disease of man or other vertebrates are known to be caused or associated with these viruses.

NPV's are currently used to only a limited extent in forestry in the U.S. This is partly due to the relatively high cost of treatment that, in some cases, makes chemical pesticides more attractive, and it is partly due to the expense of testing each new NPV before it could be registered for use against its target.

1.0 INTRODUCTION

Nucleopolyhedrosis viruses (NPV's) are naturally-occurring pathogens of insects. These viruses, sometimes called baculoviruses, are named for polyhedral inclusion bodies that are visible in the light microscope and that first appear in the nuclei of infected host cells. Nucleopolyhedrosis viruses are very host specific - each virus normally infects a single insect species or a few closely-related species. As a consequence, NPV's are prime candidates for integrated pest management (IPM) programs since they can kill insect pests without harming beneficial insects.

A number of NPV's have been isolated from nature and have been developed for use on a variety of agricultural and forest insect pests. Forest insects of the orders Hymenoptera (e.g., sawflies) and Lepidoptera (e.g., spruce budworm, Douglas fir tussock moth, forest tent caterpillar, and gypsy moth) are susceptible species. In forestry, the most successful non-chemical means of pest control has been the use of NPV's against specific sawflies, which are tree defoliators. In 1950, a low concentration of NPV that was introduced into a sawfly population in Canada became established and spread throughout the infested area. Virus epizootics* recurred for ten consecutive years and maintained the population below levels that would have caused economic damage (1). NPV's have also been used against the Douglas fir tussock moth with 90-97 percent reductions in pest populations and a significant reduction in defoliation (2). There have been many other trial applications of NPV's against forest defoliators. Table 1 summarizes the hosts, dosages used, application methods, and results of some early field tests using NPV's to control forest defoliators in North America. These results indicate that NPV application can result in high population reductions. However, the relationship between population reductions and foliage protection is unclear.

The NPV of _Heliothis zea_ has been used commercially since 1971 for control of the cotton bollworm (3). It is formulated as a wettable powder containing at least four billion polyhedral inclusion bodies (PIB) per gram

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*Epizootics refers to outbreaks of disease occurring in a large number of individuals in a population, usually associated with high host densities (1).

TABLE 1. ARTIFICIAL FIELD DISSEMINATION OF VIRUSES AGAINST SOME NORTH AMERICAN FOREST DEFOLIATORS (1)

Host	Instar treated	Dose (VIB)^a/unit	Application method^b	Results
		Nuclear-Polyhedrosis Virus		
Lepidoptera				
Choristoneura fumiferana (Clemens) (Spruce budworm)	2	$3x10^{11}$/acre^c	A	80% population reduction
	3-4	$3x10^{11}$/acre^c	A	69% population reduction
	2	0.1g/12 ft tree	G	40% infection 32 days after spray
	3-4	0.1g/12 ft tree	G	75% reduction 9 days after spray
	3-4	$3x10^9$/10 ft tree	G	28% infection 14-20 days after spray
	4	$1x10^{11}$/acre	A	54-76% population reduction Little foliage protection
Hemerocampa pseudotsugata McDunnough (Douglas-fir tussock moth)	2-3	$1x10^{11}$/acre	A	96-99.8% population reduction Foliage protection
	3-4	10^7/ml 8 ft trees heavily sprayed	G	90% mortality 24 days after spray
Malacosoma disstria Hubner (forest tent caterpillar)	1	$1.5x10^9$/tree	G	92% mortality 17-24 days after spray
	1	$1.5x10^8$/tree	G	28% mortality 17-24 days after spray
	3	$7.5x10^8$/tree	G	14% mortality 17-24 days after spray
	3-4	$2.5x10^{10}$/acre	A	no control
Malacosoma fragile (Stretch) (Great Basin tent caterpillar)	2	$2.2x10^{11}$/acre	A	70% population reduction
	1-3	$1.8x10^{10}$- $5x10^{11}$/acre	G	Some population reduction
	3-4	$5.6x10^{10}$- $2.2x10^{11}$/acre	G	Population reduction
Lymantria dispar L. (gypsy moth)	2-3	$4x10^{12}$/acre	G	Foliage protection Egg mass reduction
	1-3	$1x10^{12}$/.405 ha	G	No foliage protection
	1-3	$1x10^{12}$/.405 ha	G	Slight foliage protection Egg mass reduction

(Continued)

TABLE 1. (Continued)

Host	Instar treated	Dose (VIB)[a]/unit	Application method[b]	Results
		Nuclear-Polyhedrosis Virus		
Hymenoptera				
Neodiprion sertifer (Geoffroy) (European pine sawfly)	early instars	$6x10^{10}$/20 trees	G	100% mortality 15 days after spray
	early instars	$1.5x10^{10}$/5 acres	G	Heavy mortality 18 days after spray
	early instars	$8.3x10^{9}$/acre	A	94% mortality 21 days after spray
	1	$5x10^{10}$/acre	A	100% mortality
N. abietis (Harris) (Balsam fir sawfly)	1	$3.6x10^{7}$/2.5m tree	G	96% mortality
	3	$3.6x10^{9}$/2.5m tree	G	100% mortality
N. pratti pratti (Dyar) (pine sawfly)	early instars	$5x10^{9}$- $2x10^{10}$/acre	A	88% mortality
N. taedae linearis Ross (Loblolly pine sawfly)	1-2	$3.8x10^{10}$- $3.8x10^{11}$/acre	A	69-99% population reduction Foliage protection
N. swainei (Middleton) (Swaine's jack pine sawfly)	1-2	$1x10^{6}$/ml trees heavily sprayed	G	89-96% mortality
	1-2	$3x10^{6}$/ml trees heavily sprayed	G	80% mortality
	early instars	$3.8x10^{9}$/acre	A	100% mortality
		Granulosis Virus		
Lepidoptera				
C. fumiferana	3-4	high rate	G	61% infection
		Entomopox Virus		
C. fumiferana	2	$1.2x10^{10}$- $1.2x10^{11}$/acre[d]	A	40-61% population reduction
	3-4	$1.2x10^{10}$ $1.2x10^{11}$/acre[d]	A	57-79% population reduction No foliage protection
	4	$2.2x10^{10}$/acre	A	22% population reduction Little foliage protection

[a] VIB is Viral Inclusion Bodies.

[b] "G" refers to application with ground equipment and "A" refers to application from the air by airplane or helicopter.

[c] Contaminated with CPV.

[d] Contaminated with CPV and NPV.

of product and is applied at a rate of 2 to 4 ounces per acre (140-180 grams/hectare) (4). The sole commercial producer of this virus is Sandoz, Inc., and it is marketed under the trade name Elcar (5).

The gypsy moth NPV and the Douglas-fir tussock moth NPV are currently registered by public agencies for forest use. They are not yet commercially produced (6). The NPV of the gypsy moth is known as Gypcheck, and it is formulated as a 4 percent suspendible powder which is registered for use by or under the supervision of the U.S. Forest Service. Applications can be repeated once after 7 to 10 days. The NPV of the tussock moth is registered for application to forest trees at a rate of 0.50 ounces of formulation per acre (7). Known as TM-Biocontrol-1, it is a 3.5 percent suspendible powder for U.S. Forest Service use only. Formulations for NPV's commonly include molasses, stickers, and/or a sunscreen. The pH of the formulation must be between 5.5 and 7.5 (8).

2.0 PROPERTIES AND MODE OF ACTION

Insect viruses usually enter the host by way of the mouth or transovarially into the egg (9). Normally, larvae are infected by NPV when they feed on foliage contaminated with polyhedral inclusion bodies. In the midgut, virus invasion depends on favorable pH and digestive enzymes, and host nutrition plays a role with poor quality foliage increasing the insects' susceptibility to the virus (9). NPV contains DNA as its genetic material and multiplies exclusively in the nuclei, mainly in the skin, blood cells, fat body and trachea (10). However, in a few species, NPV's multiply only in midgut epithelial cells (10). During the infection, rod-shaped viral particles become occluded (imbedded) within polyhedral protein crystals, which are the inclusion bodies. Infected tissues liquefy as the larvae or pupae die, producing a suspension containing large quantities of infectious inclusion bodies. These can reach the soil or can contaminate foliage to give some degree of long-term pest control for some pests (2). There is considerable evidence that NPV epizootics occur in natural populations releasing much larger amounts of infectious polyhedra than those introduced by man (9).

The production of an NPV insecticide involves propagation of the virus in living host larvae. The insect cadavers can be lyophilized and ground to a powder, or they can be triturated in water, often followed by a purification process (11).

3.0 ENVIRONMENTAL FATE

NPV is not persistent on foliage, but may persist in the soil. The most important factor in the physical environment for inactivating the virus is sunlight (12). Viruses are largely inactivated within a few days after application to foliage exposed to direct sunlight. This has been demonstrated in studies on the NPV of *Trichoplusia ni* (cabbage looper) which show that deposits of the virus retain little activity five days after application to cabbage leaves exposed to sunlight (13,14). Studies on sunlight protectants indicate that deposits of viruses smeared on plants when virus-killed larvae decompose are protected substantially from sunlight inactivation because of the protein content and the dark color of the smear (15,16). Studies on the gypsy moth NPV have shown that, following application in eastern hardwood forests, it disappears from bark and foliage in 3-15 days and that normal rates of application do not significantly increase the concentration of naturally-occurring NPV in forest soil (17).

Next to sunlight, temperature is an important viral inactivator. Low mortality has been observed in infected insects exposed to low temperatures (18,19,20). Relative humidity has little effect on the inactivation of viruses but it may affect the resistance and behavior of the insect to virus infections (9). At a pH below 2, infectivity is rapidly lost.

Soil is a major site for virus persistence (9). Polyhedra can protect virions for a long time, in some cases, for several years. Consequently, large amounts of infectious polyhedra often exist in the upper layers of soil. Field tests with the NPV of *Trichoplusia ni* show that NPV retained 25 percent of its original activity six years after application (21). In addition, there are indications that the initiation of epizootics of viral disease in insect populations occurs in the soil (14,22).

No studies have been reported on the fate or persistence of NPV in water.

4.0 IMPACTS ON NON-TARGET ORGANISMS

Because of the host-specificity exhibited by NPV's, they are not expected to produce adverse impacts on non-target organisms. Ignoffo (23) has reviewed the toxicity of entomopathogenic viruses to vertebrates and found that out of 51 viruses treated in vivo, including 29 NPV, no toxicity or pathogenicity has been demonstrated. Furthermore, NPV's have never been reported to cause disease in man or in any other mammal.

4.1 IMPACTS ON BIRDS, AQUATIC FAUNA, AND HONEY BEES

No apparent adverse impacts have been observed in field studies on the effects of NPV on birds. Following aerial applications of two formulations of the gypsy moth NPV to woodland plots in Pennsylvania at a rate of 2.5 x 10^{12} PIB/ha, no short-term population changes in wild songbirds could be attributed to the virus (24). Necropsy and histopathological data on quail caged on the study plot and on 53 songbirds collected from the study plot over a 10-week period after application indicated no significant differences between control birds and treated birds.

In Ontario, Canada, the NPV of the red-headed pine sawfly was aerially applied in a formulation containing molasses and a sunlight protectant at a rate of 5.5 billion PIB/ha to two plantations of red pine (13.2 ha and 30.8 ha) (25). No adverse effects on birds, aquatic fauna (Benthic populations from a stream), or honey bees were observed.

In another study, the NPV of the spruce budworm was aerially applied to 160 hectares of infected forest on Manitoulin Island at the rate of 247.5 x 10^9 PIB/ha (26). Songbirds, small mammals, honey bees and aquatic invertebrates (bottom-dwelling fauna) were monitored. No immediate or short-term adverse impacts were detected.

Toxicity studies have also been conducted on various birds, aquatic invertebrates, and bees. Mallard hens survived five daily oral treatments with a nucleopolyhedrosis virus preparation containing 18.34 x 10^6 polyhedra/mg (dosage level: 500 mg/kg body weight) (8). The amount received over the 5-day period corresponded to the amount commonly applied to an acre of land. In feeding studies conducted using quail, mallard ducks, and blackbirds, there was no damage or death in any test organisms due to the virus (8).

Honey bees fed various NPV's in combination with sucrose at concentrations of 10^{10} polyhedra per hive showed no apparent adverse effects (8). Feeding studies of the nucleopolyhedrosis virus of H. zea carried out on juvenile oysters (Crassostrea virginica) caused no pathogenicity. Mature grass shrimp (Paldemopatas pagio) and adult brown shrimp (Penaeus estecus) were tested with the virus in suspension and showed no adverse effects or undue mortality (8).

4.2 IMPACTS ON FISH

Based on available data, no pathological effects of NPV have been observed in fish. In laboratory studies examining the potential effects of the NPV of the Douglas-fir tussock moth on salmonid fish residing in waters adjacent to the forest, the virus was found to cause no pathology in two salmonid cell lines or in three species of salmonid fish (27). The fish, Coho salmon, Chinook salmon, and steelhead trout, were exposed via three routes: waterborne exposure, intraperitoneal injection, and feeding. The virus did not persist in the fish.

Studies on pathomorphological changes in the internal organs of trout induced by NPV indicate that NPV has no lethal effect on the fish and causes no pathological changes in fish orally exposed to the virus (28).

4.3 IMPACTS ON MAMMALS

Laboratory tests have demonstrated the safety of the NPV of the red-headed pine sawfly to mammals (29). Additional reports have indicated that other NPV's also have no adverse effects on laboratory animals (31,32,33,34). Laboratory studies have also been conducted on the responses of three wild mammalian predators of the gypsy moth, the white-footed mouse, the short-tailed shrew, and the Virginia opossum, to consumption of the NPV of the gypsy moth (30). NPV appeared to have no short-term effect on the physical condition or the reproductive efficiency of the animals. There were no consistent differences in the occurrence of gross or microscopic lesions in any of the 3 species. The test animals were fed 3 formulations of the virus: (1) larvae containing between 3.5×10^8 and 6.0×10^8 PIB's; (2) purified PIB's at the rate of 1.0×10^9 PIB/animal/day for 3 days; and (3) a standard spray formulation for the gypsy moth NPV (containing Cargil insecticide base, Chevron spray sticker, IMC 90-001, water, and PIB's) at the rate of 1×10^5 PIB/animal/day for 3 days. The total amount of NPV consumed by each mouse and shrew was equivalent to more than a 40 ha exposure for a 70 kg person assuming an application rate of 5.0×10^{11} PIB/ha.

Various toxicological tests have also been performed on mammals. In acute oral toxicity tests to rats, the polyhedra of L. dispar were not toxic when administered by gastric intubation at a dose of 40×10^{19} per rat (8). Acute dermal toxicity tests on guinea pigs, eye irritation tests on rabbits, primary skin irritation tests on rabbits, and inhalation toxicity studies on rats produced no evidence of toxicity (8). In a two-year carcinogenicity study in rats, no increased mortality or tumorgenicity was found (8).

5.0 MISCELLANEOUS

NPV's appear to be good candidates for use against a number of agricultural and forest pests, but they have so far been used to only a limited extent. One barrier to the use of NPV insecticides is the host-specific property of these viruses: each NPV preparation can be expected to be effective against a single pest species. Thus, a pest must be of considerable economic importance in order to justify the large expense of meeting registration requirements for a new pesticide. A second barrier to use of NPV's is competition from chemical insecticides. However, this is not a firm barrier since the NPV insecticide for the cotton bollworm is currently being produced on a large scale at a cost that is competitive with that of chemical insecticides (5). Yet, in cases where multiple applications or high-dose applications of an NPV are required for adequate pest control, use of the NPV may never be competitive with use of chemicals when judged on purely economic grounds. Another barrier to NPV use is the expectation among some pesticide users that insects will "drop dead" immediately after being sprayed. The fact that NPV cannot produce the rapid and spectacular insect kills achieved by some chemical pesticides can lead to the perhaps erroneous perception that NPV's are less effective.

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Common Name: Pheromones, Behavior-modifying chemicals

Chemical Name: Varies

Major Trade Name: Varies

Major Applications in Forestry: Current uses limited to biosurveys and monitoring of forest insect pests.

SUMMARY

Pheromones are chemicals secreted by one insect that affect the behavior of other individuals of the same species. They are highly selective for a single (and occasionally a few closely-related) species. For forest pest management, pheromones may be used in survey traps as lures to attract insects or for population reduction and control. They are formulated in fibers or flakes for aerial application to disrupt mating. In order to be competitive with natural pheromones, synthetic behavior-modifiers must closely represent the natural chemical stimuli.

To date, most of the work with pheromones has been on a small-scale experimental basis. There are currently no operational programs using pheromones for pest control. Some of the problems associated with the use of pheromones for insect control relate to mobility of insects, spread of infestations over large areas, and difficulty in establishing effective application rates and in correlating changes in insect populations with subsequent reductions in tree damage.

There is very little data available on the environmental fate of the pheromones of forest insect pests. However, they are designed to volatilize completely and their use rates are so low that they are not expected to contaminate plant, soil, or aquatic systems. There is also little data on the effect of pheromones on non-target organisms, but because of the quantities used and the way in which the compounds are released, little impact is expected.

1.0 INTRODUCTION

1.1 BACKGROUND

Pheromones are chemicals secreted by one insect that affect the behavior of other individuals of the same species (1). Many insects use chemical communication systems that depend on the production and release of pheromones (2). Pheromones can evoke many types of behavioral responses (e.g., alarm, orientation, aggregation, mating). The sex pheromones, which induce responses such as orientation, precopulatory behavior, and mating in another individual of the same species, are considered most promising for insect control (1,3).

Basically, there are two approaches for using pheromones in forest pest management (1,2,3). First, pheromones may be used in survey traps as lures to attract insects. These traps can be useful for general survey and detection, for delimiting a population, for predicting population trends, for timing insecticide spray applications, or for post-spray surveys. Second, pheromones have been proposed for population reduction and control. This may include luring males into pheromone-baited traps (mass-trapping) or permeating the atmosphere with female pheromones which confuse the males and disrupt mating (mating disruption or "male-confusion").

Synthetic pheromones are formulated to correspond to the compositions of natural pheromones and are released at rates approximating those of the natural systems. Any changes in either the ratios of the chemical components or in the pheromone emission rates can prevent successful orientation of males to the traps. The effectiveness of a synthetic attractant in luring males is best determined by comparing the number of males caught in attractant-baited traps relative to the number of males caught in traps baited with the virgin female (3).

The forest insects for which controls via use of pheromones are currently being investigated include the spruce budworm, forest tent caterpillar, spruce coneworm, satin moth, large aspen tortrix, shoot borers, tussock moths, and gypsy moth (2). To date, most of the work with pheromones and other behavior-modifying chemicals has been on a small scale experimental basis. In only a few cases have the pheromones of forest insects been registered for use. Tables 1 and 2 list some of the behavior-modifying chemicals which have been tested for potential application in pest management.

1.2 COMMERCIAL AVAILABILITY

Behavior-modifying chemicals are produced and distributed by a number of companies. Hercon (New York, N.Y.) commercially produces "Chek/Mate", a controlled-release pheromone used to suppress and control insect pest populations by mating disruption (5). Chek/Mate consists of small pieces of laminated multi-layered polymeric dispensers ("flakes") containing the insect sex pheromone or a related behavior-modifying chemical. It is registered for use against the gypsy moth. Hercon also produces luretape, a multi-layered polymeric, laminated strip dispenser for controlled release of sex pheromones or attractants and related behavior-modifying chemicals to be used in survey and monitoring of insect populations and distributions (5).

The pheromone of the elm bark beetle, multilure, which consists of α-cubebene, 4-methyl-3-heptanol, and 2,4-dimethyl-5-ethyl-6,8-dioxabicyclo (3.2.1) octane (multistriatin), and the gypsy moth pheromone, disparlure (cis-7,8-epoxy-2-methyloctadecane) are available as luretape.

Pherocon EPSM (trans-9-dodecenyl acetate), a clear liquid used for monitoring the European pine shoot moth, is an insect attractant formulated as a rubber cap or wick by Zoecon Corp. (Palo Alto, CA). Zoecon also formulates the gypsy moth pheromone, Pherocon GM, as a cotton wick to be used for monitoring gypsy moth distributions (5).

Conrel (Needham Heights, MA) manufactures pheromone dispensers for use as lures in survey trapping and mass trapping. They consist of a parallel array of hollow plastic capillaries mounted on adhesive tape and filled with synthetic pheromone. The capillaries are open at one end to allow the attractant to slowly evaporate in air at a uniform rate (5). Conrel formulates pheromones for the elm bark beetle, the gypsy moth, and the spruce budworm (trans-11-tetradecenal: cis-11-tetradecenal) in these dispensers. Conrel currently has conditional registration on the Western pine shoot borer pheromone (6). This pheromone is for aerial application as a hollow fiber encapsulated formulation at a rate of 2 g a.i./acre (37 g total/acre) or 2 fibers/m^2.

TABLE 1. FOREST PEST SPECIES FOR WHICH ATTRACTION TO BMC'S HAS BEEN DEMONSTRATED IN FIELD TESTS (4)

Species	BMC(s)[a]	Use Pattern
Lepidoptera Lymantriidae		
Orgyia pseudotsugata	*cis*-6-heneicosen-11-one	survey
Lymantria dispar	*cis*-7,8-epoxy-2-methyloctadecane (disparlure)	
Olethreutidae		
Rhyacionia buoliana	*trans*-9-dodecenyl acetate	survey
Tortricidae		
Choristoneura fumiferana	*trans*-11-tetradecenal (sprudamone) *cis*-11-tetradecenal	survey
C. occidentalis	*trans*-11-tetradecenal *cis*-11-tetradecenal	survey
Coleoptera Scolytidae		
Dendroctonus brevicomis	*exo*-7-ethyl-5-methyl-6,8-dioxabicyclo (3.2.1) octane (*exo*-brevicomin), 1,5-dimethyl-6,8-dicoxabicyclo (3.2.1) octane (frontalin) and myrcene	survey and mass trapping
D. frontalis	frontalin and α-pinene (frontalure)	survey and baited tree with herbicide
D. ponderosae	*trans*-verbenol and α-pinene	mass trapping and baited tree treated with insecticide
D. pseudotsugae	frontalin	baited tree and removal from forest
D. rufipennis	frontalin	baited tree and removal from forest
Ips confusus	2-methyl-6-methylene-7-octen-4-ol (ipsenol), *cis*-verbenol and 2-methyl-6-methylene-2,7-octadien-4-ol (ipsdienol)	survey
I. avulsus	ipsenol and ipsdienol	survey
I. calligraphus	ipsdienol and *cis*- and *trans*-verbenol	survey
I. grandicollis	ipsenol and *trans*-verbenol	survey
I. paraconfusus	ipsenol, *cis*-verbenol and ipsdienol	survey
Gnathotrichus sulcatus	6-methyl-5-hepten-2-ol (sulcatol)	survey and mass trapping
Scolytus multistriatus	2,3-dimethyl-5-ethyl-6,8-dioxabicyclo (3.2.1) octane (multistriatin), 4-methyl-3-heptanone and α-cubebene (all 3 together called multilure)	survey and mass trapping
Hymenoptera Diprionidae		
Neodiprion lecontei	3-methyl-2-pentadecyl acetate	survey
N. swainei	3,7-dimethyl-2-pentadecyl propionate	survey

[a] BMC=Behavior-modifying chemical.

TABLE 2. FOREST PEST SPECIES FOR WHICH INTERRUPTION OF MATING OR AGGREGATION BY BMC'S HAS BEEN DEMONSTRATED IN FIELD TESTS (4)

Species	BMC(s)*	Use Pattern
Lepidoptera		
Lymantriidae		
Lymantria dispar	**2-methyl-*cis*-7-octadecene;**	**mating**
	disparlure	"
Orgyia pseudotsugata	***cis*-6-heneicosen-11-one**	"
Tortricidae		
Choristoneura fumiferana	***trans*-11-tetradecenyl acetate**	"
	***trans*-11-tetradecenol**	"
	sprudamone	"
Coleoptera		
Scolytidae		
Dendroctonus brevicomis	***trans*-verbenone; *exo*-brevicomin, frontalin, myrcene**	**aggregation**
D. frontalis	***exo*-brevicomin and verbenone;**	"
	***endo*- and *exo*- brevicomin;**	"
	frontalure	"
D. pseudotsugae	**3-methyl-2-cyclohexen-1-one (MCH);**	"
	frontalure	"
D. rufipennis	**MCH**	"
Ips paraconfusus	**verbenone**	"
I. pini	**ipsenol**	"

* See footnote in Table 1.

1.3 TECHNICAL CONSIDERATIONS IN USING PHEROMONES FOR INSECT CONTROL

Although a potential exists for use of pheromones in forestry for insect control, considerable experimental and demonstration work is needed before pheromones could be deployed on a commercial scale. At the present time, the western pine shoot borer pheromone is registered for use in mating disruption in Oregon although it has been determined that the impact of the insect is not significant, and therefore, pheromone control is not likely to be extensively used (7). Current uses of pheromones are primarily for biosurveys and monitoring, and the EPA has exempted this use from registration (8). A number of field tests which have been conducted to determine the potential use of pheromones in forest insect control are summarized in Table 3.

TABLE 3. SELECTED FIELD TESTS DEMONSTRATING THE USE OF PHEROMONES IN FOREST INSECT CONTROL

Insect Species	Pheromone	Test Area	Application	Results	Reference
Douglas-fir tussock moth (*Orygia pseudosugata*)	Z-6-heneicosen-11-one	1 ha plots	Controlled-release applicators; release rate 0.05-5.0 mg/ha/day	Disruption greater for traps baited with live females than for traps baited with synthetic. Dosages >1 mg/ha/day appeared more effective.	9
Douglas-fir tussock moth	Z-6-heneicosen-11-one	2 to 4 ha plots of white fir and ponderosa pine	Pheromone-filled Conrel fibers applied to achieve nominal dosages of 2.3, 9, and 36 g/ha	In plots with low population densities, dosages of 0, 2.3, 9, and 36 g/ha resulted in 0.26, 0.07, 0.02, and 0 egg masses/female, respectively. At higher population densities, 36 g/ha dosage resulted in 0.21 egg masses/female vs. 0.97 egg masses/female in the untreated plot.	18
White-marked tussock moth (WMT), Pine tussock moth (PTM)	Z-6-heneicosen-11-one	324 m^2 plots	Release of 140 mg/ha/day from planchet evaporators	92-100% disruption of PTM; 96-100% disruption of WMT	10
			Release rates of 20-50 mg/ha/day from hollow fiber dispensers	65-96% disruption of PTM; 76-92% disruption of WMT	
Gypsy moth (*Porthetria dispar*)	Disparlure	16 ha plots	Aerial application in microcapsules at rates of 5.0 and 15.0 g/ha	Mating suppression still evident as long as 6 weeks after application	11
Shoot borer (*Eucosma sonomana*)	4:1 cis:trans mixture of 9-dodecenyl acetate	750 ha of ponderosa pine	Hollow fibers containing 10 g a.i./ha; mean application rate 3 fibers/m^2	Damage to terminal shoots reduced 69-81% in treated areas	12
		3 plots, 3.6-8.7 ha	Aerially applied hollow fibers containing 250-300 µg pheromone; 15 g/ha nominal dosage	67% reduction in damage to terminal shoots; 79% reduction in all infested shoots. Nearly 100% disruption of female to male sex pheromone communication.	13
		0.25-5 ha of Ponderosa pine plantation	Manually applied in polyvinyl chloride strips; nominal dosages of 3.5 g/ha and 14 g/ha	Both treatments 100% in disorienting males. At 3.5 g/ha, 83% control of shoot damage and 85% population reduction. At 14 g/ha, 84.2% shoot damage control and 87.9% population reduction.	14
Western pine beetle (*Dendroctonus brevicomis*)	Mixture of (IR,5S,7R)-(+)-*exo*-brevicomin, (1S,5R)-*(-)*-frontalin, and myrcene	2.56 km^2 plots on a 65 km^2 area of Ponderosa pine	Traps containing the attractant	Tree mortality declined from 227 before the test to 73 during the suppression period	15,16
Western spruce budworm (*Choristoneura occidentalis*)	trans-11-tetradecenal cis-11-tetradecenal	350 ha	Aerial application in laminated plastic flakes at dosages of 2 and 20 g/ha	Male orientation to female-baited traps disrupted at a rate 87% in the 20 g/ha treatment.	17

Some of the potential problems which are associated with the use of pheromones for insect control relate to mobility of insects, spread of insect infestations over large areas and difficulties in establishing effective application rates and correlating changes in insect populations to any subsequent reduction in tree damage. Whether or not pheromones can be used to successfully control an insect pest depends in part on the life cycle and behavioral characteristics of the insect species. In the case of Eucosma sonomana (western pine shoot borer), three characteristics make this insect an excellent candidate for control by mating disruption (12,14): (a) the shoot borer produces only a single generation per year; (b) adults fly only 2 to 3 months during the spring; and (c) even severely infested stands harbor only about 100 adults/ha/year. It is easier to disrupt mating in low density infested areas since when populations are high, especially in a limited area, vision may be as important as pheromones for locating a mate (1). In spite of favorable characteristics for pheromone treatment, Eucosma sonomana can damage forests even in treated areas if moth flight and hence, female mating, occurs prior to pheromone application. In addition, mated females can fly into a treated area from nearby untreated areas and lay their eggs (13). The gypsy moth may be an even better candidate for mating disruption, particularly in low populations, since the female moths do not fly (19).

No protection effects have been demonstrated for any forest defoliators using behavior-modifying chemicals to interrupt mating (4). The difficulty of obtaining adequate mating disruption using pheromones is exemplified in the case of the spruce budworm. The problem with the spruce budworm is that it is an insect with a long dispersal flight (8). Some adult females deposit their eggs near the site where they fed as larvae whereas some females are dispersed miles away from the larval feeding site and deposit eggs there. If the pheromone is used at one site, some degree of disruption will occur, but in some cases, females with eggs fly in from untreated areas and lay their eggs in the treated site. In other cases, the females that disperse out of the treatment area find male moths to mate with in untreated areas (8). The pheromone would have to be applied before any mating occurred and to all areas infested with the pest in order to give adequate protection. For high density pests such as the spruce budworm, pheromones may be most effectively used as a preventive strategy in monitoring the population to determine the best time to treat an area (17).

When behavior-modifying chemicals are used in the field, it is often very difficult to correlate the resulting changes in the insect population with any subsequent tree damage (4). Although it is clear that these chemicals influence adult behavior, little information exists on the relationship between the number of adults and damage levels in the next generation (4). For some species, the precise role of male and female sex pheromones in the mating behavior of target species is poorly understood and effective pheromone application rates cannot be easily determined (2). A case in point is the control of bark beetles (D. brevicomis). When attractant release rates are increased, more bark beetles are caught and they tend to be trapped farther from the source of the attractant (15). However, higher attractant release rates also increase the tendency for host trees near the attractant source to be attacked by the beetle. The release rate, therefore, is critical - a low rate results in a low catch, whereas a high rate results in attack of the host near the attractant source (15).

2.0 PHYSICAL AND CHEMICAL PROPERTIES

The composition and the physical and chemical properties of insect behavior-modifying chemicals are highly variable. These substances are volatile organic compounds and are highly selective for a single (and occasionally a few closely-related) species (20). In order to be competitive with natural pheromones, synthetic behavior-modifiers must closely represent the natural chemical stimuli (4). The chemical structures which produce the desired response have been determined for some forest pest species and are illustrated in the following examples.

In Ips pini, only the (-) enantiomer of ipsenol interrupts its response to the naturally-produced pheromone. No activity is observed with (+)-ipsenol. In the case of the western bark beetle, D. brevicomis, no more interruption or enhancement of attraction is observed for the enantiomers of the synthetic pheromones than for the racemic compounds (22). For Scolytus multistriatus, the elm bark beetle, only one of the 4 enantiomers of synthetic 4-methyl-3-heptanol, and one of the 4 isomers of synthetic multistriatin are attractive (with (-)-α-cubebene) (23).

3.0 ENVIRONMENTAL FATE

There is very little data available on the environmental fate of the pheromones of forest insect pests. However, pheromones are designed to volatilize as completely as possible and their use rates are so low (4) that they are not expected to contaminate plant, animal, soil, or aquatic systems (15). Pheromones that are applied in hollow fibers or flakes do not ever come into contact with the environment except as a vapor (6). In addition, the low dosages and infrequent treatment make buildup of fibers and flakes unlikely (24). Some of the fibers are completely biodegradable (6).

Field experiments have demonstrated the volatility characteristics of specific forest insect pheromones. Disparlure (gypsy moth pheromone) applied to 1-ha plots as a 2 percent solution in gelatin microcapsules at a rate of 5 g a.i./ha was not detected in the field after 66 days. When a 10 percent solution was used, measurable amounts were found after 66 days (25). In aerial applications of the Eucosma sonomana sex attractant formulated in hollow fibers with 250-300 μg/fiber , the fibers were found to contain an average of 63 μg of the attractant after 85 days (13).

In studies monitoring atmospheric concentrations of the spruce budworm pheromone, a very rapid decline in atmospheric concentrations was noted (26). A hollow fiber formulation was applied at a rate of 500,000 fibers/ha to 100 ha of mixed balsam fir and white spruce in New Brunswick. Atmospheric levels dropped from greater than 7 nanograms/m^3 on the day of application to less than 1 nanogram/m^3 one week following application.

The fate of pheromones in soil and water has been studied in agricultural applications. Methyl Eugenol, the attractant of the oriented fruit fly, dissipated rapidly from soil and water (27). The half-life was 6 hours in both soil and water at 32°C. At 22°C the half-life in soil was 16 hours and in water, 34 hours. It did not leach in the three soils tested. Only 3.8 percent of the pheromone was recovered from the surface of field-grown tomatoes after 24 hours. In another study, gossyplure [(Z,Z) and (Z,E)-7,11-hexadecadiene-1-ol acetate], the pink bollworm pheromone, was found to have a half-life in soil of 24 hours (28). The half-life in water was 7 days.

In soil column tests, no leaching was found. In soil, the acetate was hydrolyzed to the corresponding alcohol.

4.0 IMPACTS ON NON-TARGET ORGANISMS

Few studies are available on the effect of pheromones on non-target organisms. However, because of the amount used and the way in which the compounds are released, very little impact on non-target organisms is expected.

In field tests, application of the Douglas-fir tussock moth pheromone (Z-6-heneicosen-11-one) did not result in reduced parasitism of fertile tussock moth eggs masses by two major egg parasites, *Telenomus californicus* and *Tetrastichus* (29). The pheromone was applied in Conrel fibers to a 4-ha plot at a rate of 36 g/ha.

Laboratory toxicity evaluations show no adverse effects on test animals exposed to the *Eucosma sonomana* pheromone (30). Test animals were exposed by inhalation to 4 g volatilized pheromone in one hour. This dose is equivalent to the total amount of pheromone vaporized in one acre of pine plantation during a 10-week period following application. No adverse effects were observed. At an oral dose of 15 g/kg, no deaths or abnormalities were noted in rats. Rabbits had no adverse reactions to a dermal dose of 3 g/kg. The pheromone was found to be a slight to moderate eye irritant only.

The attractants of the western pine beetle, exo-brevicomin and frontalin, are non-toxic as determined in acute oral and dermal tests, eye and skin irritation tests, and inhalation tests in laboratory animals (15). In the field, however, non-target flying insects, bats, and small birds can be physically caught and die in sticky traps (15).

5.0 MISCELLANEOUS

The progress in developing and using pheromones in forestry has been slow due to the high cost of research and the complexities involved in research on the dynamics of highly mobile, widely distributed pest populations (20). The costs involved with trying to develop, register, and introduce a pheromone for mating disruption on a commercial scale include synthesis, formulation research development, efficacy testing, development of residue analytical methods, radiochemical synthesis, study of environmental chemistry and effects, toxicology, and process development and manufacturing (31).

Such costs have been estimated at about $1.5 million (31). In addition, there are two major problems which seriously hinder large scale use of pheromones (31):

1. Risk of failure by the developer to secure government approval or registration, and
2. Uncertainty of the grower in risking use of a new material for protection of valuable crops.

A third difficulty is that there is a low market potential because of the high specificity of a pheromone for a pest (20).

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